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Copper Sensor System for Unattended Marine Operations II: Development of a Polymer Sensor and Field Tests

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13. ABSTRACT (Maximum 200 words) A major source of trace metal contamination in the marine environment is the copper containing anti-fouling paints on ship hulls. This research examines the potential of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine=BCP) embedded in the polymer, Nafion 117, for use as a reliable chemical for developing a sensor capable of measuring copper(I) in seawater. The sensor must have: 1) parts per billion (ppb) detection limits; 2) capable of operation in marine environments; 3) the ability to detect copper(I) within 17% of measurements made with the Standard Method BCS procedure. The use of the polymer with Bathocuproine (BCP) allows for a rapid electronic measurement. This electronic measurement uses optical fibers running from a small spectrophotometer to either a flow through or a submersible device containing the BCP impregnated polymer. Response times for the devices depend on the size of the membrane used and the flow rate. The flow cell takes eight minutes to reach a peak optical density while the submersible probe takes one minute. Nafion 117 polymer impregnated with Bathocuproine (BCP) is a rapid method used for detecting copper(I) released into the marine environment.					
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Copper Sensor System for Unattended Marine Operations II: Development of a Polymer Sensor and Field Tests

Executive Summary

A major source of trace metal contamination in the marine environment comes from the copper containing anti-fouling paints on ship hulls. This study tests the hypothesis that the organic molecule, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine=BCP) attached to the polymer Nafion 117 is a reliable chemical for developing a sensor capable of measuring Cu(I) in seawater. The purpose is to develop a sensor system that will measure Cu (I) contamination quickly. The sensor must have

- parts per billion (ppb) detection limits,
- marine environmental immersion capability, and
- the ability to detect the copper(I) oxidation state.

An easily and readily deployed sensor can yield results that will allow the deployment of remedial methods to avert an environmental problem.

The developed sensor uses the perfluorinated ionomeric film, Nafion 117. This film has a Teflon matrix with sulfate side groups that facilitates the BCP/copper reaction. When the Nafion 117 membrane with the imbedded BCP is exposed to Cu(I), it will turn a shade of orange corresponding to the Cu(I) concentration. The developed Cu(I) concentration on the membrane is readable with a comparator, with a fiber optic sensor or with a colorimeter.

In the marine environment, anti-fouling paint containing Cu(I) presents a challenge because it is designed to leach continuously over a period of time. The Cu(I) is a biocide that kills or prevents attachment of organisms to a ship hull, but, also is a pollutional source.

The conclusions from this second phase of the study are:

- that the chemical procedure using the BCP impregnated Nafion 117 membranes affords a probe to test for total available ionic copper [(I) and (II)],
- that the chemical procedures used are reproducible and robust,
- that the environment plays a major role in the distribution of total available ionic Cu [(I) and (II)],
- that the Nafion 117 membrane impregnated with BCP adequately and accurately detects Cu(I), and
- that there is a knowledge base for continuing and expanding the studies.

In all instances, the field use of the Nafion 117 membrane impregnated with BCP was a useful and rapid analysis tool.

This study is the second phase in a program designed to develop an easily used and dependable sensor for detecting copper(I) in the marine environment. Further field testing, testing of thinner Nafion polymers, other probe configurations, and recommendations of methods to reduce the Cu(I) loading to the environment are under study.

Copper Sensor System for Unattended Marine Operations II: Development of a Polymer Sensor and Field Tests

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ABSTRACT

A major source of trace metal contamination in the marine environment is the copper containing anti-fouling paints on ship hulls. This research examines the potential of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine =BCP) embedded in the polymer, Nafion 117, for use as a reliable chemical for developing a sensor capable of measuring Cu(I) in seawater. The sensor must have

- parts per billion (ppb) detection limits,
- marine environmental immersion capability, and
- the ability to detect the Cu(I) oxidation state.

Results of this study show the Nafion 117 containing BCP measures Cu(I) within 17% of measurements made with the Standard Method BCS procedure. The use of the polymer with Bathocuproine (BCP) allows for a rapid electronic measurement. This electronic measurement uses optical fibers running from a small spectrophotometer to either a flow through or a submersible device containing the BCP impregnated polymer. Response times for the devices depend on the size of the membrane used and the flow rate. The flow cell takes 8 minutes to reach a peak optical density while the submersible probe takes 1 minute. Nafion 117 polymer impregnated with Bathocuproine (BCP) is a rapid method useful for detecting Cu(I) released into the marine environment.

Key Words: Optical Sensor, Bathocuproine (BCP), Copper, Anti-fouling Paint, Nafion 117.

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INTRODUCTION

Being able to operate unrestricted in all navigable waters and maintain a world presence, is the highest priority of the U. S. Navy. International treaties and more stringent environmental laws impact on the Navy's ability to maintain a presence in the world and at home. With the future implementation of the Uniform National Discharge Standards (UNDS), the ability to quickly and easily measure Cu(I) as well as total ionic copper [Cu(I) and (II)] is paramount. Compliance with these treaties and laws minimizes fines and impacts operational restrictions. The Navy's stated environmental goals are:

- to demonstrate leadership in the Federal sector by complying with Federal, state and local environmental regulations and laws;
- to prevent pollution at Navy activities;
- to cleanup shore activities where past waste disposal practices are potentially hazardous;
- to provide stewardship for natural resources on Navy activities; and
- to promote environmental protection and natural resource stewardship (NAVFAC 1998).

The use of copper leaching or ablating anti-fouling hull coatings presents a possible pollution problem.

Presently, to operate in a relative cost effective manner all Navy ships use an anti-fouling hull coating. The majority of navy ships use an anti-fouling coating containing copper. Copper can create pollution problems for non-fouling species like marine fishes (Sindemann 1996). Therefore, the purpose of this work is to develop a sensor system for use in the marine environment that can detect the initial release form of copper [Cu(I)].

Anti-fouling coatings prevent some and reduce other organisms (barnacles, seaweeds, tubeworms, etc.) from attaching to ship hulls. It prevents the step-wise fouling of a hull. This fouling can add to the vessel's operational cost (Figure 1). With organism attachment to a ship hull, comes increased drag and thus increased fuel consumption during passage through the water (Claisse and Alzieu 1993)(Figure 1). Wynne and Guard (1997) report that under certain conditions a ship having a 24 month biofilm can "... require 8% more shaft horsepower to move as fast as (a) comparable ship with no biofilm." Biofouling increases fuel consumption between 18 and 22% for U. S. Naval ships (Wynne and Guard 1997). The copper based anti-fouling coating is an attempt to reduce and control the fouling of the vessel. Because commercial vessels and pleasure craft are also using copper anti-fouling coatings, there is a potential for toxic loading of the aquatic environment. Nriagu (1979) reports that a major source of copper [initially Cu(I)] in the marine environment is from anti-fouling paints on ship hulls. Thus, this research focuses on a way to detect the levels of available ionic copper [Cu(I) and (II)] in the marine and estuarine (brackish) water environment.

To detect the available ionic copper, we use the water insoluble organic molecule, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine = BCP). It is a dye chemical that reacts quickly with Cu(I). Since it is a dye and the copper affects a color change (shades of orange), it may be possible to use it for developing a fiber optic sensor system for use in marine environmental applications.

The marine environment is not just the water adjacent to a ship hull. It is, also, the water upstream and downstream of the hull, the water column and the sediments. Pore water, the water in the sediment, is a large source of trace metals like copper (Nriagu 1979). Therefore, dredging operations in naval harbors can potentially re-introduce copper to the water column and create a remediation problem (Scanferlato and Cairns 1990).

Any trace metal sensor system designed for use in the marine environment must have

- ppb detection limits,
- in-situ operation capability, and
- the ability to detect the Cu(I) oxidation state.

In this work, the effort will be on the development of a simple to use and inexpensive Cu(I) sensor with field testing in an estuarine environment.

Copper in the Environment

Many researchers have noted the potential toxic effects of trace metals (Sorensen 1995, Vymazal 1995, and Newman and McIntosh 1991). This report will not review the voluminous literature other than to note that the effects of copper are both beneficial and costly to plants and animals. Because copper is a biologically essential element, studying it is more difficult than a none essential trace metal like lead or mercury. Copper remains the primary "biocide" ingredient in anti-fouling hull coatings on Navy ships. The copper leaches or ablates from the hull coating, and is a potentially toxic trace metal waste. Once in the environment, the copper, because of high reactivity, quickly interacts with organic and inorganic ligands (Figure 2).

As a toxic substance, it will eliminate aquatic biota until

- dilution,
- dissipation,
- chemical change, or
- volatilization

reduces the toxic concentrations below some population's and individual's response threshold. The result is tolerant species, and/or contaminated food resources, and elimination of populations.

On the hull of a ship, a surface area is readily available for colonizing. This colonization is biofouling and it is what the anti-fouling coating is designed to retard.

Biofouling is a stepwise procedure (Figure 3). It begins with the unfouled surface being conditioned chemically and the formation of an organic film (Little 1984, Loeb and Neihoff 1975, Baier 1972). This film "wets" the unfouled surface making it more attractive for colonization by bacteria (Dexter et al 1975, Dexter 1978). Once the surface is organically "wet" then bacteria can attach (reversible sorption) but are removed easily (Marshall 1976, Marshall et al 1971). As soon as the bacteria form extracellular bridging polymers (irreversible sorption), the primary biofouling film forms (Little 1984). This primary film becomes attractive to algae and protozoa as well as attracting detritus and corrosion products (Little 1984). With the algae and protozoa in the fouling film, the next steps are the attraction of animals like barnacles and tube worms (Figure 1).

Any unfouled surface placed in the marine environment invites colonization. This colonization occurs slowly or rapidly depending on the ambient temperature. In essence, the entire biofouling process is an ecological succession process (Odum 1971). The initial biofilm and bacteria stages are pioneer succession and the later progression through algal and protozoan inhabitation are serene stages (stepwise changes) until the biofouling film reaches a climax where if you scrape off a barnacle what will grow back is a barnacle. Anti-fouling coatings are an attempt to stop or at least slow down this process on any structure or vessel placed in marine waters.

METHODS

In a previous report, Lamontagne et al (1998) discussed the procedures necessary for determining ionic copper with quick and useful analyses. The initial work (Lamontagne et al 1998) focused on the aqueous reaction of Cu (I) with an organic molecule that would develop a reproducible color in proportion to the amount of Cu (I) complexed. To effect this reaction and make the measurement, they tested the primary organic reactants

- 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Figure 4A)
(Bathocuproinedisulfonic acid=BCP), and
- 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid
(Figure 4B) (Bathocuproinedisulfonic acid=BCS).

The first test procedure is the Bathocuprione Method outlined in Standard Methods (Greenberg et al. 1992). This aqueous procedure is the control test method used to compare sensor/probe response. The BCS/BCP reaction with Cu(I) produces an orange color that is measurable with a spectrophotometer at 484nm (Figure 5A), or a Klett-Summerson Colorimeter (Figure 5B) using a green filter in the range 470-500nm. According to Leckie and Davis (1979), the unique property of Cu(I) is its ability to form organometallic bonds so reaction with the BCS/BCP dye is rapid.

A single Cu(I) molecule reacts with 2 BCS or BCP molecules (Diehl and Smith 1972). The BCS/BCP molecules, due to steric hindrance, are at right

angles to each other and the nitrogen molecules are exposed. Cu (I) bonds between the nitrogens and creates the orange color (Figure 6).

To establish the quantity of Cu(I) and Cu(II) in the water samples water a differential procedure was used. To measure for Cu(I) only BCS was added to the sample. In a second sample, the complete BCS Standard Method with the hydroxylamine hydrochloride reductant was added and the total ionic copper concentration measured. The difference between the values obtained with the complete Standard Method and with just BCS is Cu(II).

Instrument Calibration

The calibration procedure for all analytical instruments used in the study involved preparing a standard curve for each device (spectrophotometer - Figure 7, and colorimeter - Figure 8). These initial procedures used both de-ionized water and water of varying salinity. In each type of water (brackish water, seawater, deionized water) known amounts of Cu(II) were added in the following parts per billion (ppb=mg/L) concentrations, 5 ppb; 10 ppb; 25 ppb; 50 ppb; 100 ppb; 500 ppb; 1000 ppb. The seawater had a salinity (parts per thousand = ppt) of 35.2ppt, a pH of 7.8 and a temperature of 25 C. Deionized water had a 0ppt salinity, a pH of 6.6 and a temperature of 25 C. Dilutions of the seawater gave two brackish water values of 8.8ppt and 17.6ppt. These dilutions were for use in the field testing.

The reliability of the calibration curves were tested with known standards of 50 and 100 ppb of Cu(II). All testing used standard copper concentrations prepared from dilutions of a 1000 mg/ml Cu(II) standard in 2% nitric acid (SPEX Industries, Inc.) (Lamontagne et al 1998).

Figure 7 is a calibration curve for the Hitachi Scanning Spectrophotometer for each of the salinities. The light path for the scanning spectrophotometer is 10 cm. In Figure 8, are the curves for the Klett-Summerson Colorimeter. The light path here is 4.4 cm (largest cell available). Klett-Summerson optical readings are convertible to absorbance (optical density) by multiplying with the factor 10^{-2} . Figure 9 is a comparison of the standard curves for both instruments. The Klett-Summerson Colorimeter is the device used in the copper sensor field testing.

The experimental probe tested in the field was made from Nafion 117 membranes (an ionomeric polymer) imbedded with a chelating ligand(Figure 10). This ionomeric membrane formed the matrix for the chemical reaction in the probe. The ligand was BCP, an hydrophobic dye reagent. After exposure, the absorbance values for the membranes was obtained using a 1.3 cm diameter cell in the Klett/Summerson colorimeter.

Figure 11 is a comparison of the results from the two path lengths used in the field colorimeter. The shorter path length is for the membranes as it allows the membrane to be closer to the light source. The curve for the smaller cell is similar to the cell with the longer path length.

Testing Water

The initial seawater used in all procedures is from 2000m deep in the Sargasso Sea (pH = 7.8; salinity = 35.2 ppt; temperature = 25.0 C). This water tested free of detectable copper trace metal. It was filtered using 0.45m Millipore filters to remove organisms and particles larger than 0.45 microns. The filtration set-up used a water trap to prevent any back flushing of tap water during filtering. Storage of the filtered water was in nitric acid cleaned bottles.

Distilled water was from tap water passed through a Millipore, Inc. Milli-Q and Milli-RO deionization system and analyzed for the presence of copper.

Cleaning of all glassware was with a 10% solution of nitric acid. Distilled water rinsed glassware went into a nitric acid cleaning solution overnight, rinsed in the Millipore deionized water and soaked for 24 hours in Millipore deionized water before drying and storage. There was a periodic check of all experimental water and glassware for contamination by copper.

Probe Development

Previous efforts by the authors showed that the use of BCP hydrophobically bound to a C18 polymeric resin and then immobilized onto the ends of two optical fibers and allowed to air dry to form a sphere of approximately 1 mm in diameter could give a response to Cu(I) in solution (Ervin et al 1993; Ewing et al 1998). Although this work provided proof of concept, probe engineering was inadequate and response times were slow due to diffusion rate limitations. The present work builds upon this earlier work by using the Nafion 117 membrane and is divided into 3 major objectives:

- (1) development and testing of a dosimeter type probe that would indicate levels of copper (I) contamination in the environment;
- (2) improving probe design;
- (3) expanding sensing capability of probe to detect both Cu(I) and Cu(II).

This report describes the first objective along with field test data.

The probe is a perfluorinated ionomeric film matrix (Nafion 117) that supports the BCP reagent. Structurally, the film is comprised of a Teflon backbone having sulfate side groups (Figure 10). As an ionomer, it has both hydrophilic and hydrophobic sites. It is expected that the BCP molecules reside within the hydrophobic site. The procedure for imbedding the BCP into the 2 x 3cm Nafion 117 strips used in the field test is as follows:

- (1) Cut Nafion film into usable strips (2 x 3 cm).
- (2) Place Nafion film strips into 1 molar nitric acid.
- (3) Boil the Nafion strip in nitric acid for 0.5 hr.
- (4) Remove strip and rinse with deionized water.
- (5) Soak strip for 12 hours (overnight) in deionized water.

- (6) Prepare 10^{-3} (0.001) molar solution of bathocuproine (BCP) in 100% ethanol.
- (7) Obtain small screw cap vials and fill with BCP/ethanol.
- (8) Place one strip of nitric acid boiled Nafion into each vial with the BCP/ethanol solution.
- (9) Leave strip in vial for 24 hr.
- (10) After 24 hr. remove strip and rinse in deionized water.
- (11) Place strip in 1000 ppb Copper(I) solution (500 ppb copper standard in 50ml deionized water + 1ml 50% HCl + 5ml hydroxylamine hydrochloride + 5ml sodium acetate [see *Standard Methods*]).
- (12) Leave strip in Cu solution for 6-24 hours. The membrane will turn orange.
- (13) Remove the strip, rinse in deionized water, remove color in 1 molar nitric acid (1hr); remove and rinse strip in deionized water.
- (14) Store preconditioned BCP/Nafion strips in deionized water until use.
- (15) To regenerate strip after use, place in 1 molar nitric acid until color fades, rinse in deionized water and store in fresh deionized water until re-use.

Experimental Devices

Once activated with BCP, the membranes received testing in both the laboratory and the field. Calibration of the membranes followed the same procedure as that for water samples. The calibration device for the membranes was the Klett-Summerson Colorimeter using the 1.3 cm light path cell (Figure 11). In addition to the calibration curves for the membranes, it was necessary to establish a response time (Figure 12).

Three different configurations were designed to house the membrane:

- (1) a dipping holder (Figure 13);
- (2) a non-submersible flow through chamber (Figure 14); and
- (3) a submersible flow through chamber (Figure 15).

Each device was tested first under laboratory conditions and response curves developed (Figures 16, 17, and 18). The devices tested during this field test were the dipping holder and the non-submersible flow through chamber. Primarily, testing was on the reaction of the membrane irrespective of the holder. In most instances, the dipping holder was the primary test vehicle.

Field Study

For this study, two marinas having vessels using copper based anti-fouling paints were selected. The marinas are located the Severn River sub-estuary of the Chesapeake Bay (Figure 19). This is a tidally influenced area and as such, each marina flushes water in and out on the flood and ebb tides. The tides for this area are semi-diurnal with a mean amplitude of 0.6m.

Formulas used to calculate flushing time (number of tidal cycles estimated to flush the water volume) in the marina is $T = (V + P)/P$ (Dyer 1973) where T is the number of cycles; V is the low tide volume of the marina and P is the tidal prism volume (amount of water brought in and out on the tide). Water exchanged on each tide is estimated from the formula $R = [P/(V + P)]100$ (Dyer 1973) where R is the exchange ratio in percent. The water stability in the basins is derived from calculating the Richardson number (type of flow) and the Reynolds number (stratification) (Dyer 1973). Finally, the particle settling velocity was computed to estimate the residence time for a copper contaminated particle. The equation used was $v = 2.66 \times 10^4 (r^2)$ where v is in cm per second and r is the radius of the particle (Williams 1962).

In addition to the tidal influence, climatological data was obtained from the National Climatic Data Center of the National Ocean and Atmospheric Administration. This included temperature anomalies for the study period to determine climatic normality and weather radar (NEXRAD) images to indicate presence and absence of storms. The depth of the stirring by wind was calculated using the Ekman formula where $D_E = 7.6W(\sin F)^{1/2}$. The value D_E is the Ekman depth (maximum wind influenced depth), F is the latitude, and W is the wind speed in m/sec (Foerster and Thompson 1985).

Salinity is partly a function of the chloride concentration. These chlorides stabilize the copper(I) coming from the anti-foulant coating (Moffett and Zika 1983; Forstner and Whittmann 1979). Chloride concentration in the marinas was determined from the equation $S = 1.80655 \times Cl$, where S is the salinity in parts per thousand (ppt) and Cl is the chloride in ppt (Weyl 1970). Salinity measurements were from a Seabird CTD System, Model #SBE19 (conductivity, salinity, temperature, depth). Finally, density of the water column in the Severn sub-estuary during the field study was calculated using the UNESCO 15 parameter equation (Pond and Picard 1975). This equation was programmed into a Microsoft Excel 5.0 spreadsheet and the calculations performed. All densities were converted to the Sigma-T (σ_t) function to express the density as a whole number with the equation $\sigma_t = (\text{density} - 1)1000$ (Pond and Picard 1975).

Figure 20 shows the two basins studied. The basins are at the U.S. Naval Academy on the Severn River, Chesapeake Bay, Annapolis, Maryland. The Yard Patrol craft (YP) basin (Figure 20A) is 25000 m² in surface area and accommodates 20, 33.3m Yard Patrol Craft having an individual leaching surface area of 361 m² for a total copper leaching area of 7220 m² (Figure 21). This is 29% of the mean water area of the basin and at a leach rate of 1.1-1.5 ppb/cm²/hr (Lamontagne et al 1998) is an estimated total mean copper input of 2527 kg/day in a dilution volume of 100000 m³. This basin circulates with the Severn River through its entrance (Figure 22A).

The other small harbor studied was Santee Basin where the Naval Academy keeps 13.4 meter sailboats (Figure 20B). The sailboat basin is 5575 m² in surface area and accommodates 20 sailboats having an individual leaching surface area of 139 m² for a total copper leaching area of all vessels of

2780 m² (Figure 23). This is 50% of the mean water area of the basin. At a leach rate of 1.1-1.5 ppb/cm²/hr (Lamontagne et al 1998), this is an estimated total mean copper input of 861 kg/day in a dilution volume of 16725 m³. This basin circulates with the Severn River through its entrance and under the riverside piers (Figure 22B).

Water samples came from various points within the two basins (Figure 24) at the surface, at mid-depth and at the bottom. Water sampling was with a cleaned horizontal Niskin water sampler (Figure 25). In addition to water samples, sediment samples were taken for copper analysis using a hand deployed, short barrel, plastic lined, coring device. Sampling stations included areas adjacent to the vessels, areas remote from the vessels, and at the basin entrances. In addition, water was taken from the basins on both the flood tide and the ebb tide. Salinity, temperature, and tide movement in addition to ionic copper [both Cu(I) and Cu(II)] were the environmental parameters sampled. A Seabird CTD System Model #SBE19 (conductivity, salinity, temperature, depth) sampled and recorded a vertical profile for each sampling date (October 30-31, and November 13-15, 1997).

To assure the quality of the water and sediment collections, all water sample collection containers were chemically cleaned in nitric acid, rinsed and a 1% nitric acid solution left inside. The sediments were collected with a 15 cm long by 5 cm wide hand deployed plastic coring device. The samples were placed immediately into certified (Eagle Pitcher Environmental Services) 113 gram, glass, lined screw cap and chemically cleaned collection jars. The sediment samples were held for laboratory analysis for copper using proton induced x-ray emission (PIXE) (Figure 26).

Next, a study of the copper complexation capability of the Severn River was estimated experimentally. Water samples prepared from mixing Sargasso Sea water and deionized water to achieve a salinity of 17.6ppt, were spiked with Cu (I) and Cu (II). The copper was obtained from soaking coupons (Lamontagne et al 1998) coated with Woolsey Neptune Red anti-foulant paint (what is used on the hulls of vessels in both marinas). These water samples were mixed with natural levels of suspended solids (26 - 33 mg/l) filtered from the Severn River using pre-weighed 0.45m Millipore filters. The samples were incubated at 25 C and harvested at 0, 1, 2, 3, 4, 5, 24, 48, 72 hours, and the concentration of Cu(I) and Cu(II) measured.

Finally, 250 ml portions of each water sample taken from both basins were filtered through pre-weighed 0.45m Millipore filters. The filtered solids were weighed and the distribution of suspended sediment mapped.

RESULTS AND DISCUSSION

Standardization Tests

The goal of this study was the development of a robust, accurate and precise method to measure copper in the marine/estuarine environment. As a reference, the Standard Method developed by Smith and Wilkins (1953) and codified by nationwide testing in the handbook *Standard Methods for the Examination of Water and Waste Water* (Greenberg et al. 1992) was selected. Figure 8 were the curves derived from multiple testing of with Standard Method. Both distilled water and water of varying salinities, received testing and yielded similar results.

The probe being developed used Nafion 117 ionomeric membranes impregnated with BCP. Each water sample from the two basins was measured using both the Standard Method as a reference and the Nafion Membrane Method. Results of the comparison between the reference analysis and the membrane analysis (Figure 27) showed that the membrane method reads within 17% Standard Method..

Comparison of the curves in Figures 8, 9, and 10 demonstrates a method that:

- reads in the low ppb range,
- reads in the high ppb range,
- gives similar results in chemically different water,
- appears chemically robust, and
- produces a reasonable agreement with Beer's Law (Hemond and Fechner 1994) over concentration range of 10 - 2000 ppb (Lamontagne et al 1998).

Field Test

The field test was a way to assess the measuring capability of the probe designed and tested in the laboratory. In addition, it was an opportunity to develop information on the distribution of available ionic copper in basins containing copper antifoulant hull coatings of the same type (Woolsey Neptune Red - copper leaching).

As discussed previously, water sample analyses were on water collected from 2 marina basins at the United States Naval Academy, Annapolis, Maryland (Figure 20). Field testing of the BCS/BCP methods occurred on October 30-31, 1997, and repeated on November 13-15, 1997. These dates allowed for a study of the copper concentrations in the sailboat basin with sailboats (Oct.) and without (Nov.). The two marinas provided us with access to basins with a ready source of exposed anti-fouling surface; similar depths; controlled access; but with different circulation patterns.

During this study the weather was slightly warmer than normal in October and temperatures in November were seasonally normal (Figure 28). October in the study area was slightly dryer than normal and November was slightly wetter (Figure 29). Prior to the October sampling (3 days), a rain storm moved through the area (Figure 30). There were no rain storms immediately before the November sampling. This is reflected in the salinity measurements (Figures 31B and 32B)

Table 1 is a summary of the tidal influences occurring within each marina. The semi-diurnal tides take an estimated number of cycles to completely flush each basin. As the basin flushes each cycle, only a percentage of the copper contaminated water is removed. The water not exchanged with the Severn River is re-circulated and mixed and available for further exchange on the next cycle. This flushing and exchange dilutes and removes copper contamination from the marinas. In general, the data estimates that it will take almost 4 days to flush the YP Basin and about 3 days to flush the Sailboat Basin. The exchange ratio estimates that 13% and 17% respectively of the basin's water actually flushes on a tidal cycle. These are slow exchanges so the opportunity to retain available ionic copper long enough for it to complex with suspended matter exists. Sediment rates (Table 1) are rapid (seconds) for the particles in the size range of sand (2 mm) and extremely slow for clay (0.0002 mm). This indicates some compelled copper will remain in the basin while other is flushed. According to Miffed and Seiko (1983), the chloride concentrations (Table 1) may assist in holding the copper(I) in solution.

During the field test, the basins had laminar flow (Richardson Number) and lacked stratification (Reynolds Number). The ebb tide seemed to have more of a mixing effect on the Sailboat basin as indicated by the stability (potential for vertical movement) and Richardson number. Mixing appeared to be better in the Sailboat Basin. What these values mean is that the total available ionic copper can be useful in tracing the circulation within and flushing from the basins (Table 1).

At the time of this study the water column over the depth of the marina basins was uniform in density (St) (Figures 31A and 32A). During this Fall time period, this implies no vertical stratification and no barrier to vertical mixing. Figures 31B and 32B demonstrate the trends for the salinity and temperature which are functions of the density. The pattern is relatively uniform over the depths of the marina basins. Depths over 4 meters (YP) and 3 meters (SB) are found in the Severn River. This indicates that bottom current flows will be affected by the shoaling at the entrance to the two basins. Enhanced mixing may occur as the water passes up and over the sills.

A wind between 0.5 m/sec and 1.0 m/sec (1-2 kts) would induce stirring of the basins to the bottom (Figure 33). The wind and tidal stirring during this period of low vertical stratification would insure easy mixing and transport. Horizontal stratification appears as a function of tidal forcing.

Ionic Copper Distribution

Copper in its ionic forms of Cu(I) and Cu(II), available copper, appears to complex quickly in the aquatic environment (Zirino and Yamamoto 1972, Steemann Nielsen and Wium-Andersen 1970, Alexander and Corcoran 1967). Measurement, therefore, must occur soon after collection. Laboratory studies show that Cu(I) changes to Cu(II) in 16 hours. In addition, the Cu(II) becomes complexed with available ligands within 48 hours (copper in samples containing 26-33mg/l of particulate matter). Therefore, a pierside laboratory was used for this field test. The laboratory was at the United States Naval Academy next to the Santee Basin (sailboat) (Figure 34).

Figure 34 shows the distribution of Cu(I) on the ebb tide in Santee Basin. This basin freely flushes to the Severn River so isochem lines appear drawn out with the ebbing water. These lines, also, appear to have a clockwise rotation component on the ebb. Cu(I) is highest in the area around the sailboat moorings.

Figure 35 is the distribution of Cu(I) on the ebb tide in the Yard Patrol Craft Basin. Cu(I) is 93% of the total available ionic copper. This basin has a bulkhead under the mooring pier and water circulates in and out through a single opening. The isochem lines in this basin appear to be moving toward the opening in a counterclockwise rotation with the higher concentrations pulled away from the moorings.

Figure 36 is a comparison of total available ionic copper [Cu (I) + Cu (II)] distributed in Santee Basin during both ebb and flood tides. The total available ionic copper during the flood tide is only Cu(II) because the sailboats were removed three days before. Testing shows Cu(I) as negative. The isochem lines show the pull out/push in motion with more of a mixing/concentration on the flood and a dilution on the ebb. Theoretically, less dense water moves into the basin on the ebb while more dense water pushes in on the flood. The area at this time of year exhibits a vertically mixed profile (Figure 31).

Figure 37 is a comparison of total available ionic copper [Cu(I) + Cu(II)] distributed in the Yard Patrol Craft Basin during both ebb [Cu(I)] and flood tides [Cu(I) + Cu(II)]. The isochem lines show the pull out/push in motion with the tide. The 40 and 50 ppb isochems on the ebb tide are due most likely to the action of Yard patrol craft maneuvering in the central part of the basin. No maneuvers occurred during sampling on the flood tide.

Figure 38 is a vertical profile of total available ionic copper [in this instance it is Cu(II) - sailboats were removed], through the center of Santee Basin. The copper present is probably from copper leaching from treated pier pilings and bulkheads since no sailboats are at the moorings.

Figure 39 is a vertical profile of the total available ionic copper [Cu (I) + Cu (II)] in the Yard Patrol Craft Basin. The cross section is through the middle of the basin. Data reflects a more uniform vertical mixing. The higher values on the right include probably include both hull and bulkhead leaching, while the

concentration on the left is at the entrance of the marine railway where a vessel was moored.

The 6 figures (34 -39) demonstrate several facts resulting from using the Membrane Method:

1. Cu(I) and Cu(II) existed in the waters of the 2 basins.
2. highest concentration of total available copper during the flood tide are along the bottom and under the moorings indicating water displacement to the interior of the basins (in and around in clockwise motion in the YP Basin and in under the riverside pier in a counterclockwise motion in the Sailboat Basin) and dilution by the incoming tidal prism volume.
3. higher concentrations of total available copper exist in Santee Basin which appears to reflect the copper treated mooring piers and bulkheads because the sailboats were absent.
4. environmental physical parameters (tides, wind, current, salinity) play a major role in eluting, suspending, and circulating the total available ionic copper.
5. the membrane probe was useful in measuring the changes in total available ionic copper in the basins.

Complexed Copper

Each basin received water containing suspended solids (plankton, sediments, organic debris). Since total available ionic copper complexes readily with organic matter (Leckie and Davis 1979), the processes of adsorption, absorption and complexation were estimated to be present. To estimate the effect of suspended sediments on total available ionic copper, several analyses were run. In the first set of analyses, Cu(I and II) were introduced into samples containing 26-33 mg/L of suspended material (normal for the 2 marinas) and allowed to stand for a maximum of 72 hours. After the first 16 hours, Cu(I) disappeared. Thirty two hours later (48 hours from start of test) Cu (II) was gone. The next analysis was for the distribution of suspended matter in the 2 marina basins. Figure 40 and 41 are the suspended solids distributed in the 2 basins on the flood tide. These suspended solids have the capability of attracting total available ionic copper and the potential to either transport the complexed copper out of the basins or to settle it to the bottom.

A proton induced x-ray emissions (PIXE) system was used to test for bound copper in the sediments in each basin. The results showed little concentration in the sediments (Figure 42) except in the areas of low circulation. The PIXE system accurately measures in the parts per million (mg/L) range so this initial analysis does not determine if the other sampled areas had parts per billion (ug/L) concentrations. What the results do show is the distribution of a "hot spot" for copper accumulation. For both areas, the samples (YP and SB basins) are in sediments on the outside edge of the eddy-like circulation

pattern. The SB basin (Figure 42B, Station 1) area was behind a short bulkhead where water movement would be slow and thus sedimentation in this zone is higher. In the YP basin (Figure 42A, Station 26) the higher region is in a corner where circulation is slower and there is an abandoned marine railway. What these results imply is that the circulation in the basins are important in flushing total available ionic copper.

CONCLUSIONS

Total available ionic Copper [(I) and (II)] is a potentially toxic trace metal controlled in the marine/estuarine environment by the chemistry of the water column (pH, salinity, ligands) and physical factors (currents, dilution, tides, suspended sediments). Thus anti-fouling paint containing Cu(I) presents a challenge to the environment because its design is to leach continuously over a period of time. The copper is a biocide that kills or prevents attachment of organisms to a ship hull, but, also, becomes a source of introduced Cu(I) and eventually Cu(II) to the environment.

The conclusions from this phase of the study are:

- that the analytical procedure based upon the BCP impregnated Nafion 117 membranes affords a robust probe which can detect total available ionic Cu[(I) and (II)];
- that the chemical procedures are reproducible and rapid (min);
- that the technique provided validation that the environment plays a major role in the distribution of total available ionic copper.

Further field testing in ship yards, testing of thinner polymers and other probe configurations, are all necessary.

ACKNOWLEDGMENTS

The team expresses their gratitude to the Oceanography Department of the United States Naval Academy, Captain Dennis Whitford USN, Chair, for the use of their Hendrix Oceanography Laboratory on the Severn River. In addition, we, also, appreciate the excellent technical support provided by the Oceanography Department Laboratory Director Mr. Douglas Smith. Finally, the team expresses its thanks to Mr. James Aisquith for his assistance in sampling, equipment rigging, and boat handling, and Mr. Kenny Zepp for electronics and data retrieval support. These people and facilities allowed us the opportunity to concentrate on the sampling mission and the field test, while they provided us the logistical support. In addition, we express our thanks to Patricia Thompson of the Johns Hopkins University Applied Physics Laboratory for assistance with developing the density calculations using the Microsoft Excel 5.0 spreadsheet. Finally, we appreciate the assistance of Jeff Vanhoy and Douglas Edsall of the Physics Department at the Naval Academy for the analyses using the PIXE system.

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Table 1. Tidal influence in the two marina basins.

PARAMETER	YP BASIN	SAILBOAT BASIN
<i>BASIN VOLUME</i>	100000 m ³	16735 m ³
<i>TIDAL PRISM VOLUME</i>	15000 m ³	3345 m ³
<i>FLUSHING TIME</i>	7.7 tidal cycles	6.0 tidal cycles
<i>EXCHANGE RATIO</i>	13%	17%
<i>PARTICLE SETTLING VELOCITY</i> ¹	975 DAYS (CLAY) TO 9.75 X 10 ⁻⁴ DAYS (SAND AND DETRITUS)	731 DAYS (CLAY) TO 7.31 ⁻⁴ DAYS (SAND AND DETRITUS)
<i>RICHARDSON NUMBER</i>	Oct. = 1.025 x 10 ⁻⁴ (water column turbulent) Nov. = 1.353 x 10 ⁻⁴ (water column turbulent)	Oct. = -998.00 x 10 ⁻⁴ (water column turbulent) Nov. = 35.3 x 10 ⁻⁴ (water column turbulent)
<i>REYNOLDS NUMBER</i>	1.515 LAMINAR FLOW	1.136 LAMINAR FLOW
<i>STABILITY</i>	Oct. = 15.69 x 10 ⁻⁴ (water column stable) Nov. = 2.07 x 10 ⁻⁴ (water column stable)	Oct. = -36.66 x 10 ⁻⁴ (water column unstable) Nov. = 1.03 x 10 ⁻⁴ (water column stable)
<i>MEAN CHLORIDE CONCENTRATION</i>	Oct.=4.82 ppt Nov.=5.29 ppt	Oct.=4.82 ppt Nov.=5.29 ppt

1. Settling velocity is calculated assuming a current vector trajectory of 45° for a particle range from clay (0.0002mm) to sand and organic detritus (2.00mm).

FIGURE CAPTIONS

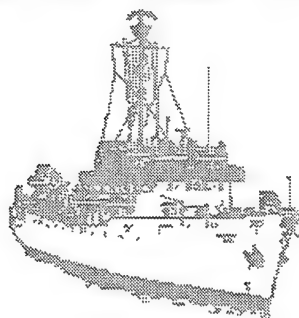


Figure 1. Problems created by increased biofouling on ship hulls. Tubeworms are a problem in subtropical and tropical marine environments.

Figure 2. Movement of ionic copper through the aqueous marine environment. there are many pathways by which copper can move and react.

Figure 3. The formation of a complex biofilm has many stages. Each stage affects the operational characteristics of a vessel underway.

Figure 4. The forms of the bathocuproine dye molecule used measure Cu (I). The dye plus Cu (I) yields an orange color. A. Water insoluble form. B. Water soluble form.

Figure 5. The optical instruments used to measure the intensity of the orange color produced in the BCP/BCS reaction with Cu(I).

Figure 6. There are two molecules of either BCP or BCS needed to react with Cu(I). Due to steric hindrance the molecules are at right angles to each other and trap a Cu(I) molecule between them.

Figure 7. Calibration curves for the Hitachi scanning spectrophotometer at different salinities.

Figure 8. Calibration curves for the Klett-Summerson colorimeter at different salinities.

Figure 9. Comparison of the spectrophotometer and the colorimeter standard curves at 35.2 parts per thousand (ppt) salinity.

Figure 10. The structure of the Nafion 117 membrane (A). It is a perfluorinated ionomer. The backbone is Teflon. Included is an example of a membrane (B) with a developed BCP-Cu(I) complex (orange streak on membrane), and a structural model (C) (re-imaged from Eisenberg and Yeager 1982).

Figure 11. Comparison of standard curves produced by the two different sizes of cells used with the colorimeter. The larger cell is for aqueous samples and the smaller cell is for use with the Nafion membranes.

Figure 12. Response of Nafion membranes to different concentrations of Cu (I). Linearity decreases above a concentration of 1000 ppb.

Figure 13. The copper testor (test orange) tested in the field trials. It holds a 2 x 3 cm Nafion 117 film impregnated with BCP.

Figure 14. A machined stainless steel flow through cell with Teflon insert to hold Nafion 117 membrane. Water pumps through this device and Cu(I) reacts with the BCP impregnated in the membrane. The absorbance (optical density) is read by a spectrophotometer equipped with fiber optics.

Figure 15. A machined polyethylene flow through cell. The modified fiber optic cable holds a small disk of Nafion 117 impregnated with BCP. Water pumps through this device and Cu(I) reacts with the impregnated BCP. Absorbance is read by a spectrophotometer.

Figure 16. The dipping probe response time takes between 15 and 20 minutes to develop the membrane. The size of the membrane is larger so an operator can see the color. Once developed the color is stable.

Figure 17. The non-submergible flow through cell response time takes between 8 and 10 minutes to develop the membrane. The size of the membrane is smaller than the dipping probe. Once developed the color is stable.

Figure 18. The submergible flow through cell response time takes 1 minute to develop the membrane. The size of the membrane is the smallest of the three membrane holders. Once developed the color is stable.

Figure 19. The Chesapeake Bay study area. Both marinas are in close proximity to each other.

Figure 20. Water level views of the two marinas showing moorings and vessel types. A. YP basin (Annapolis Naval harbor). B. Sailboat Basin (Santee Basin).

Figure 21. The Yard Patrol craft is a vessel class. It is wooden hulled, 34.5m long, and powered by two diesel engines driving twin screws.

Figure 22. The two marinas showing mean water depths. (A) YP Basin. (B) Sailboat Basin.

Figure 23. Santee Basin showing the 13.4m sailboats. These vessels are fiberglass hulled and have an auxiliary diesel engine with a single screw.

Figure 24. The two marinas showing sampling sites. Sampling sites include water for both horizontal (surface) and at 1m and 3m depths. Some sample sites include bottom sediment samples. (A) YP Basin. (B) Sailboat Basin.

Figure 25. The Niskin horizontal water sampler.

Figure 26. A schematic of the Proton Induced X-ray Emissions (PIXE) system used for copper complexed in the bottom sediments. (A) an example of the read-out from the instrument, (B) a schematic of the instrument.

Figure 27. A comparison of the membrane method for measuring Cu(I) with the aqueous Standard Method. This is a comparison based on the mean of the water samples containing 50 ppb Cu(II).

Figure 28. Satellite temperature anomalies for the period of study (October-November, 1997). October was a month slightly above normal for temperature. November was a month average for temperature.

Figure 29. Satellite wetness anomalies for the period of study (October-November, 1997). October was a month slightly below normal for wetness. November was a month slightly above average for wetness.

Figure 30. Weather radar 86 (NEXRAD) mosaic data for the period before the October samplings. A storm moved through the area before the field test, but was dry during the field test. No data is available prior to the November test but it was also dry during the field test.

Figure 31. Water Density (st) during the October field test (A) with a comparison of the salinity and temperature data (B). These readings were taken in the Severn River between the 2 marinas. The water column is not vertically stratified at the depths of the marinas so tidal water is free to circulate.

Figure 32. Water Density (st) during the November field test (A) with a comparison of the salinity and temperature data (B). These readings were taken in the Severn River between the 2 marinas. The water column is not vertically stratified at the depths of the marinas so tidal water is free to circulate.

Figure 33. Potential wind effect on the two basins. Winds of 0.5-1.0m/sec (1-2 kts) will enhance stirring of the basins to the bottom.

Figure 34. Horizontal Cu(I) distribution in Santee Basin during ebb tide. The isochem lines show a clockwise rotation of the water as it moves out on the tide.

Figure 35. Horizontal Cu(I) distribution in the YP Basin during ebb tide. The isochem lines show a counterclockwise rotation of the water as it moves out on the tide.

Figure 36. Horizontal total available ionic copper[(I) and (II)] distribution in Santee Basin during the ebb and flood tides. The isochem lines show a clockwise rotation of the water as it ebbs and a counterclockwise rotation during flood.

Figure 37. Horizontal total available ionic copper[(I) and (II)] distribution in the YP Basin during the ebb and flood tides. The isochem lines show a counterclockwise rotation of the water as it ebbs and a clockwise rotation during flood.

Figure 38. Vertical total available ionic copper[(I) and (II)] distribution in Santee Basin during the flood tide. The isochem lines show water pressed against the pilings and bulkheads. The pilings and bulkheads are treated with copper. No sailboats were in the basin.

Figure 39. Vertical total available ionic copper[(I) and (II)] distribution in the YP Basin during the flood tide. The isochem lines show water under the boats to have higher concentrations. A higher concentration exists in the surface water off the marine railway that has a YP moored.

Figure 40. Horizontal distribution of suspended solids in Santee Basin on the flood tide. Again the motion is a counterclockwise inflow with the majority of the solids carried in water coming in under the pier.

Figure 41. Horizontal distribution of suspended solids in the YP Basin on the flood tide. Again, the motion is a clockwise inflow with the majority of the solids carried in water coming in through the opening to the Severn River.

Figure 42. Results of sediment samples analyzed by PIXE for complexed copper. Both basins have a "hot spot" area where copper in the parts per million (ppm) range is accumulating. These areas are spaces on the outside (slower) of the tidal rotational eddy in the basin.

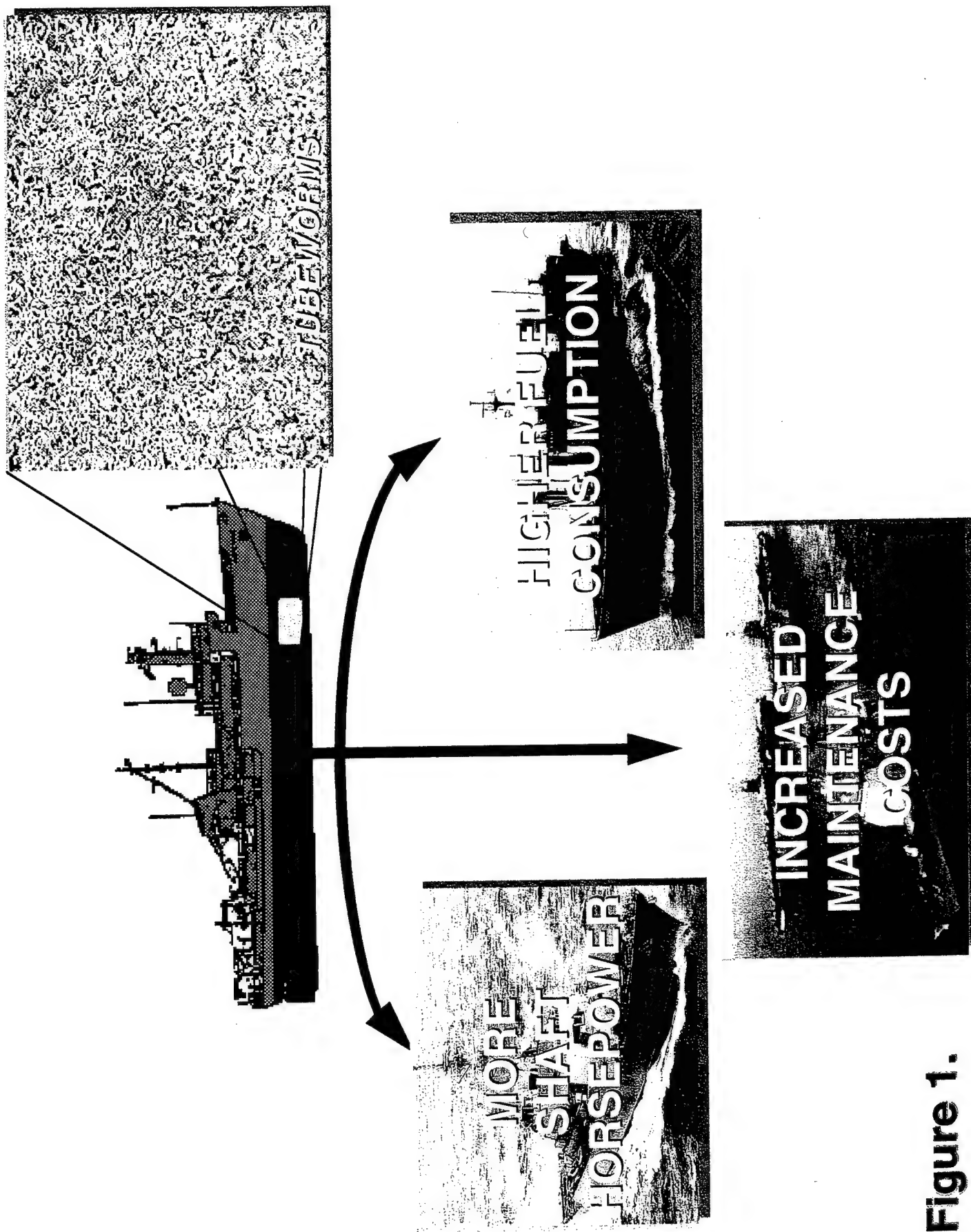


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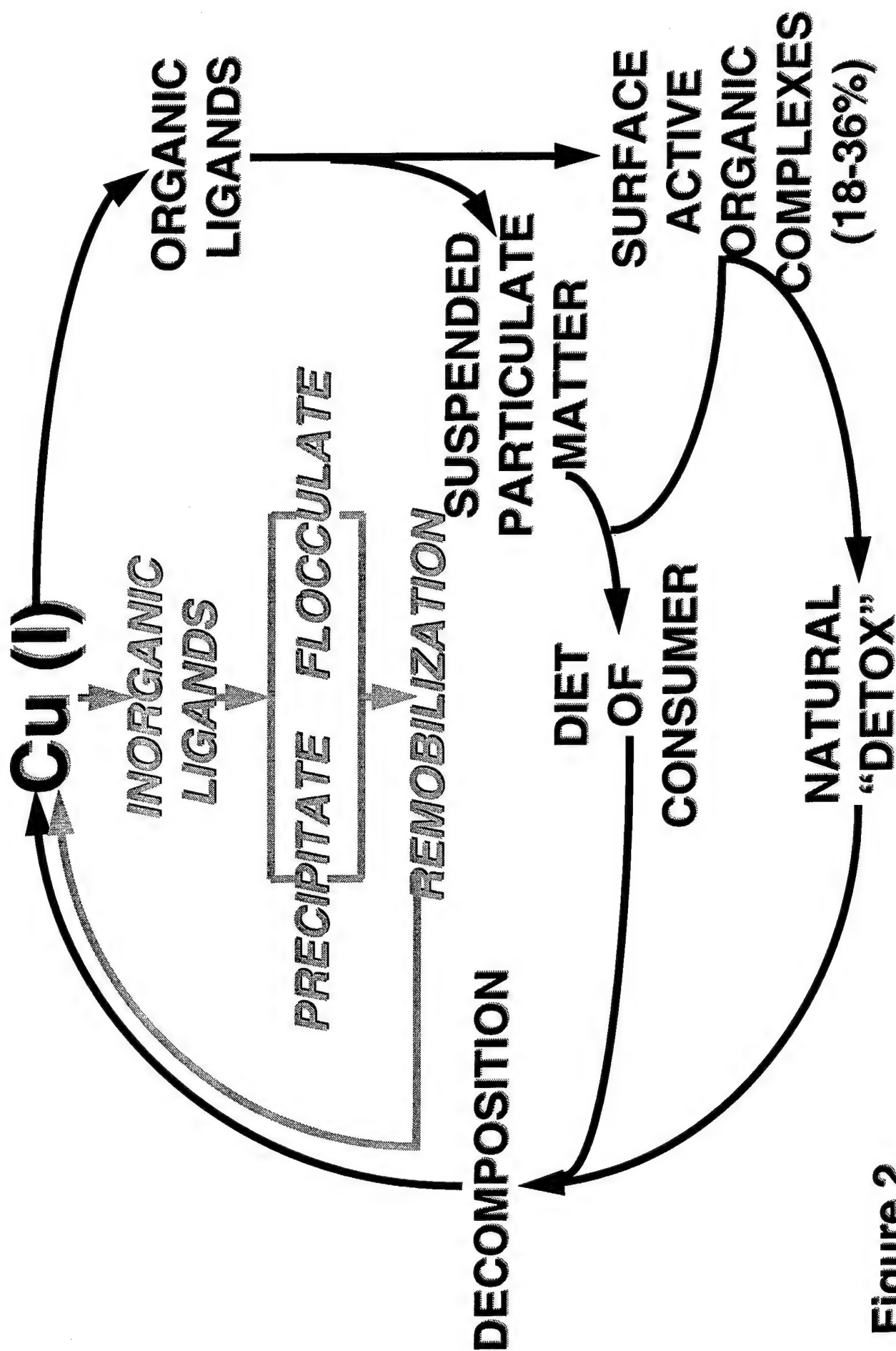


Figure 2.

Figure 3.

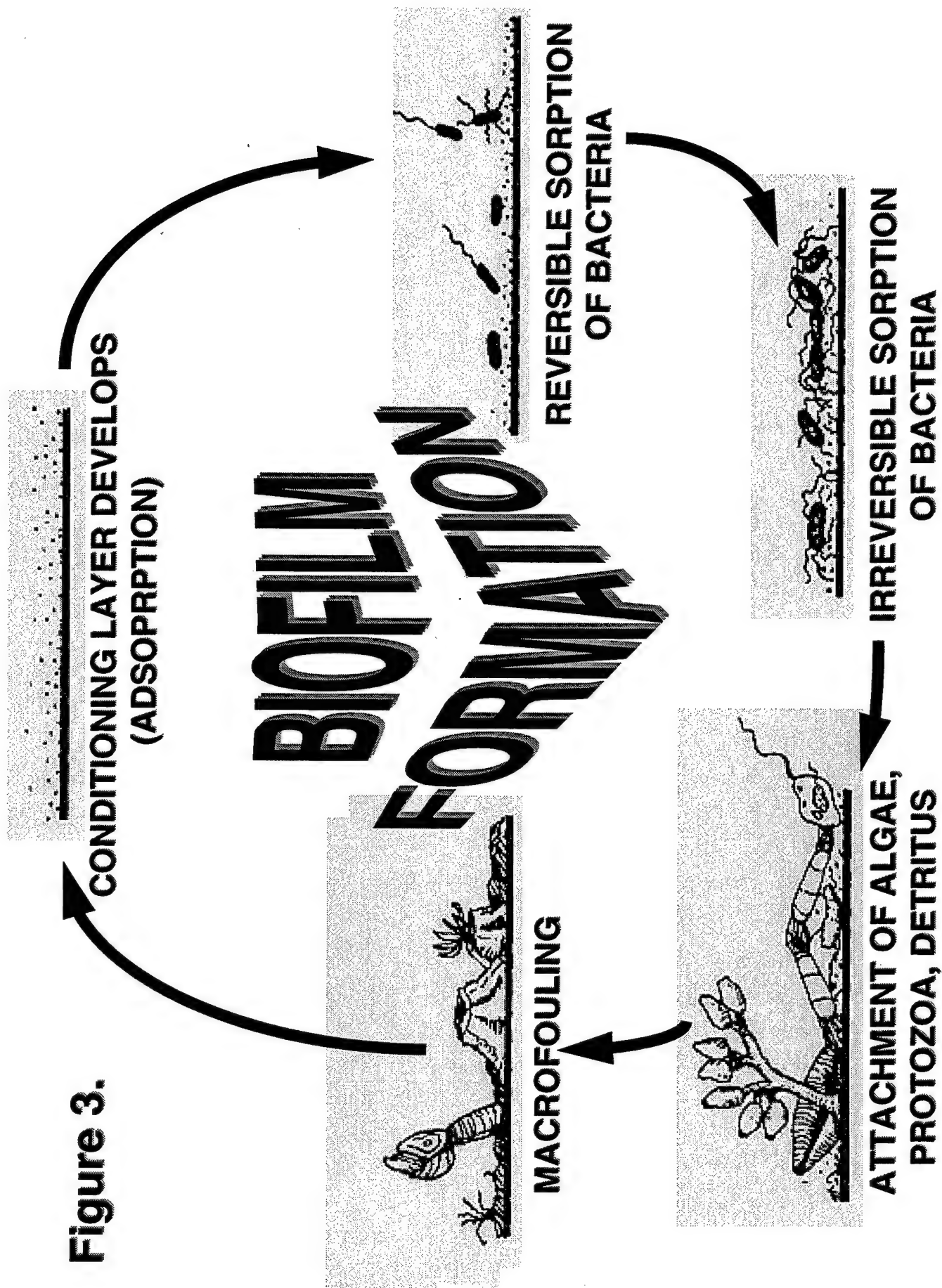
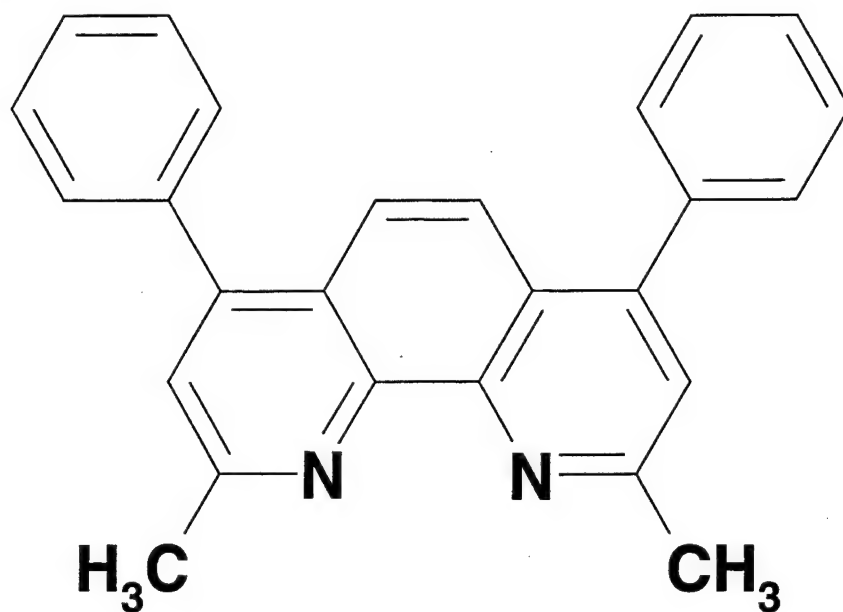
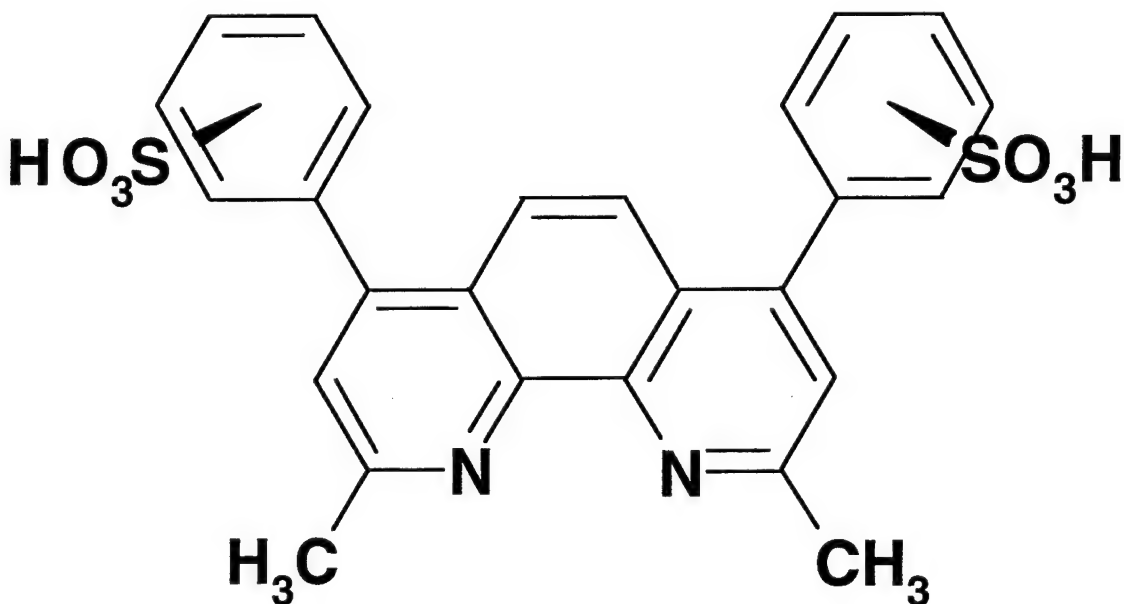


Figure 4.



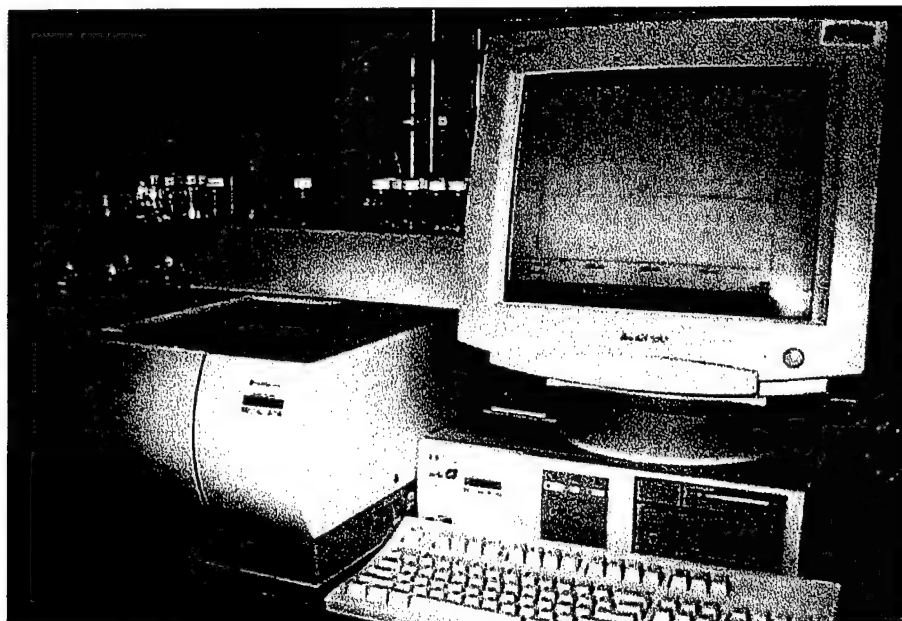
A.

2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
Bathocuproine (BCP)



B.

2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline disulfonic acid
Bathocuproine (BCS)



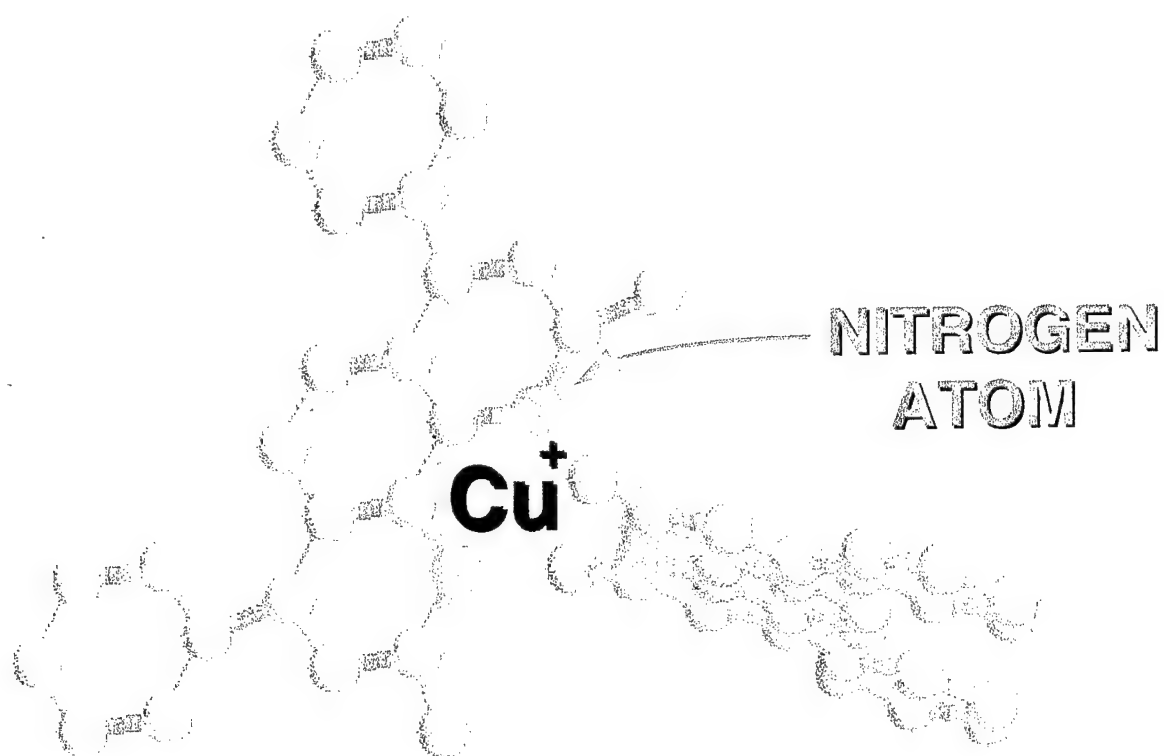
A. **Hitachi Scanning Spectrophotometer**



B. **Klett/Summerson Colorimeter**

Figure 5.

Figure 6.



**BATHOCUPROINE
(BCP)**

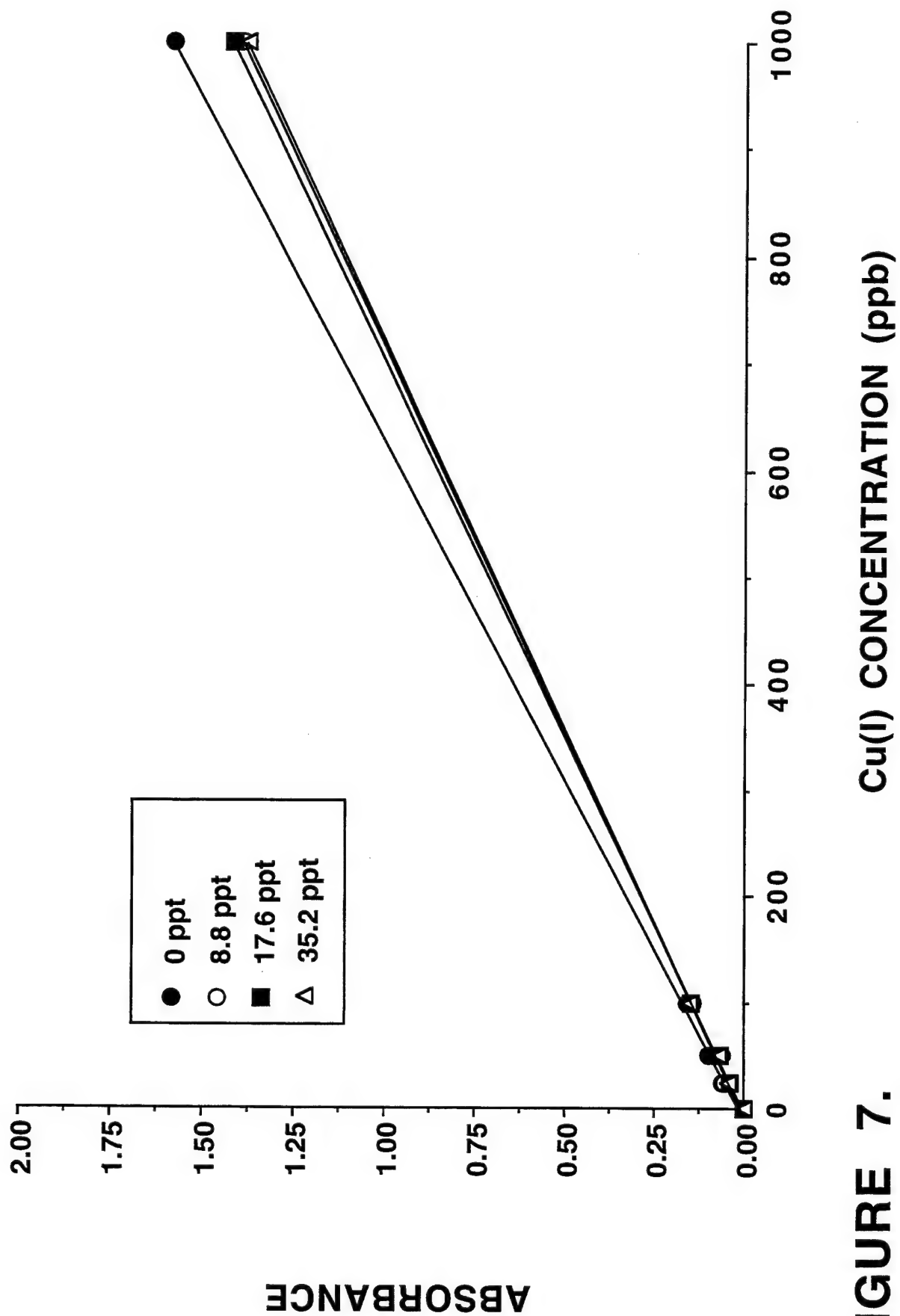


FIGURE 7.

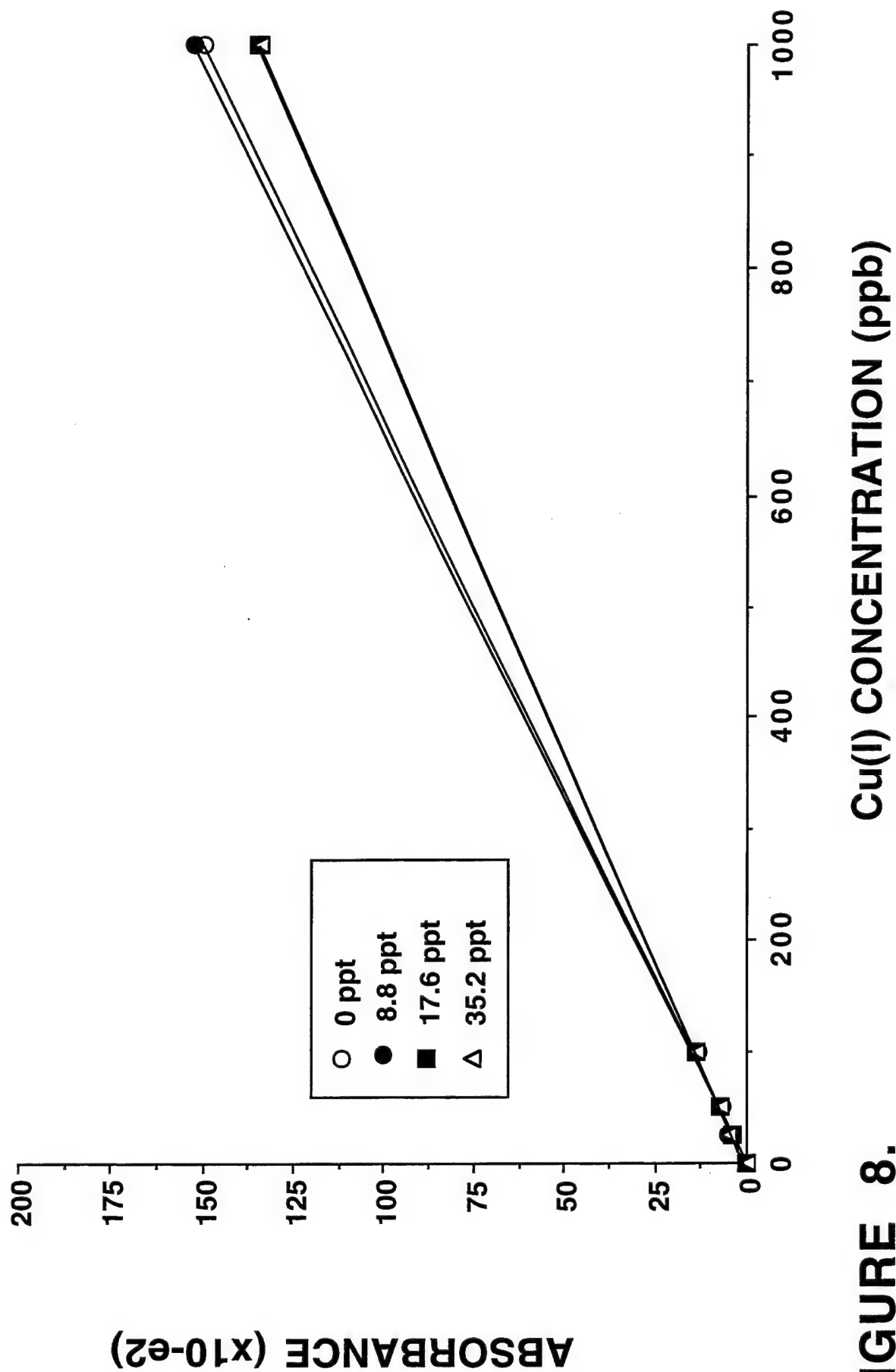


FIGURE 8.

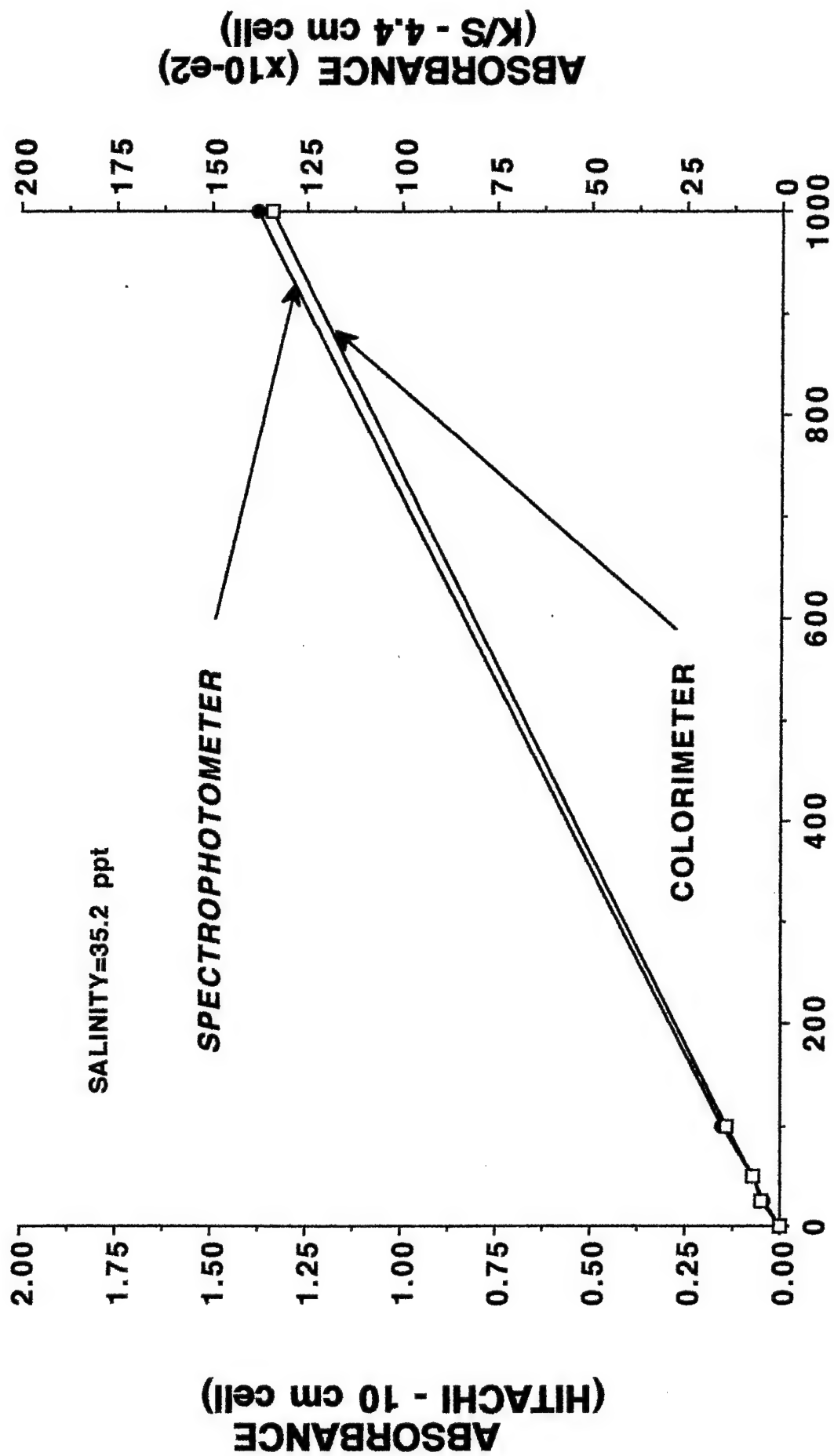


FIGURE 9. Cu(I) CONCENTRATION (ppb)

TEFLON BACKBONE

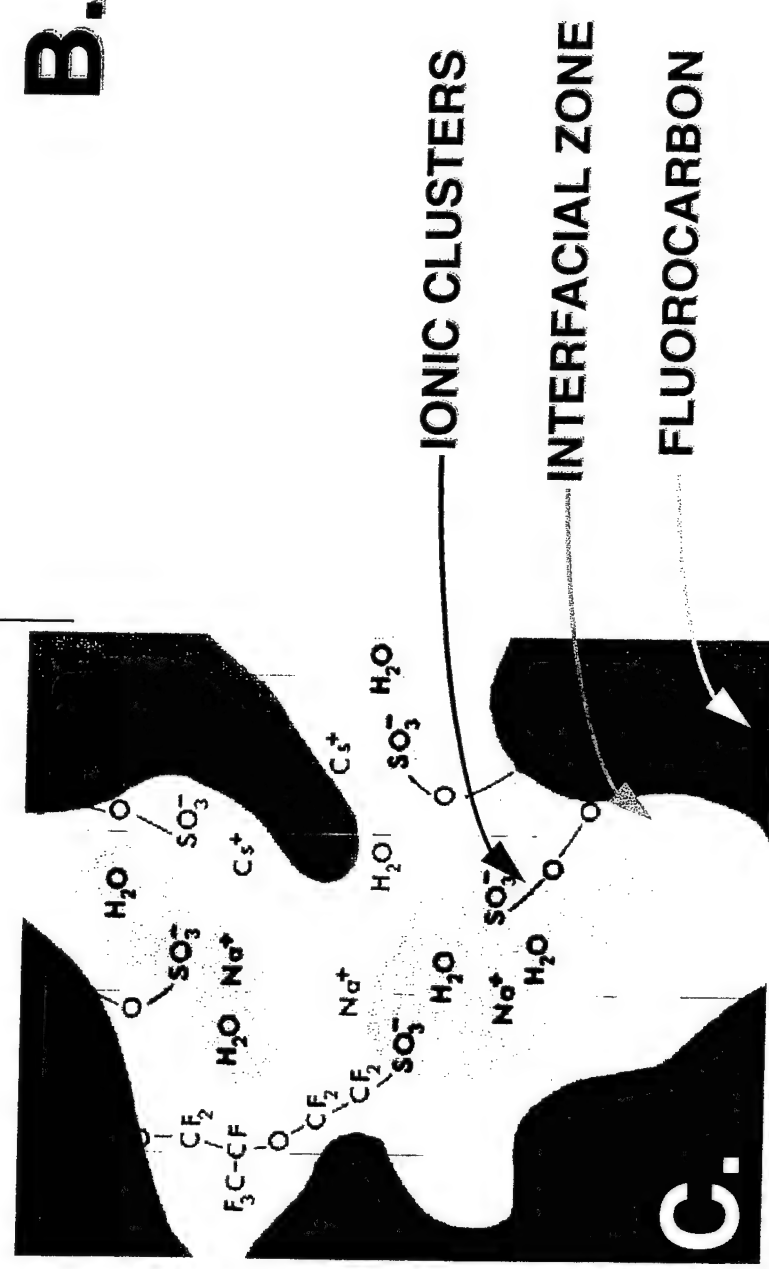
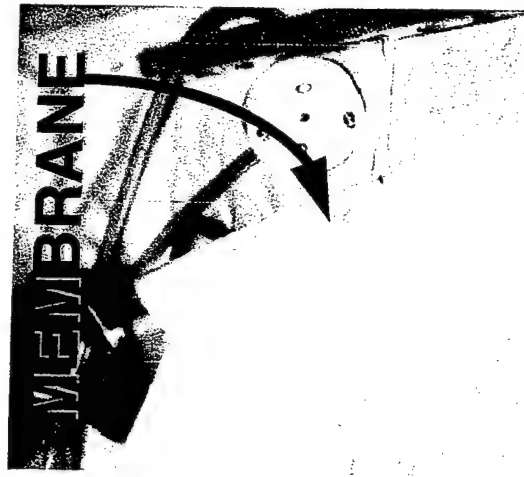
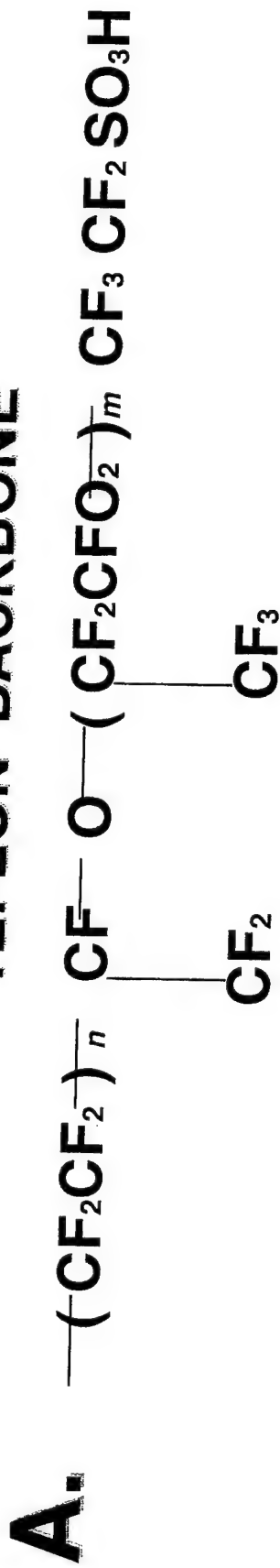


Figure 10.

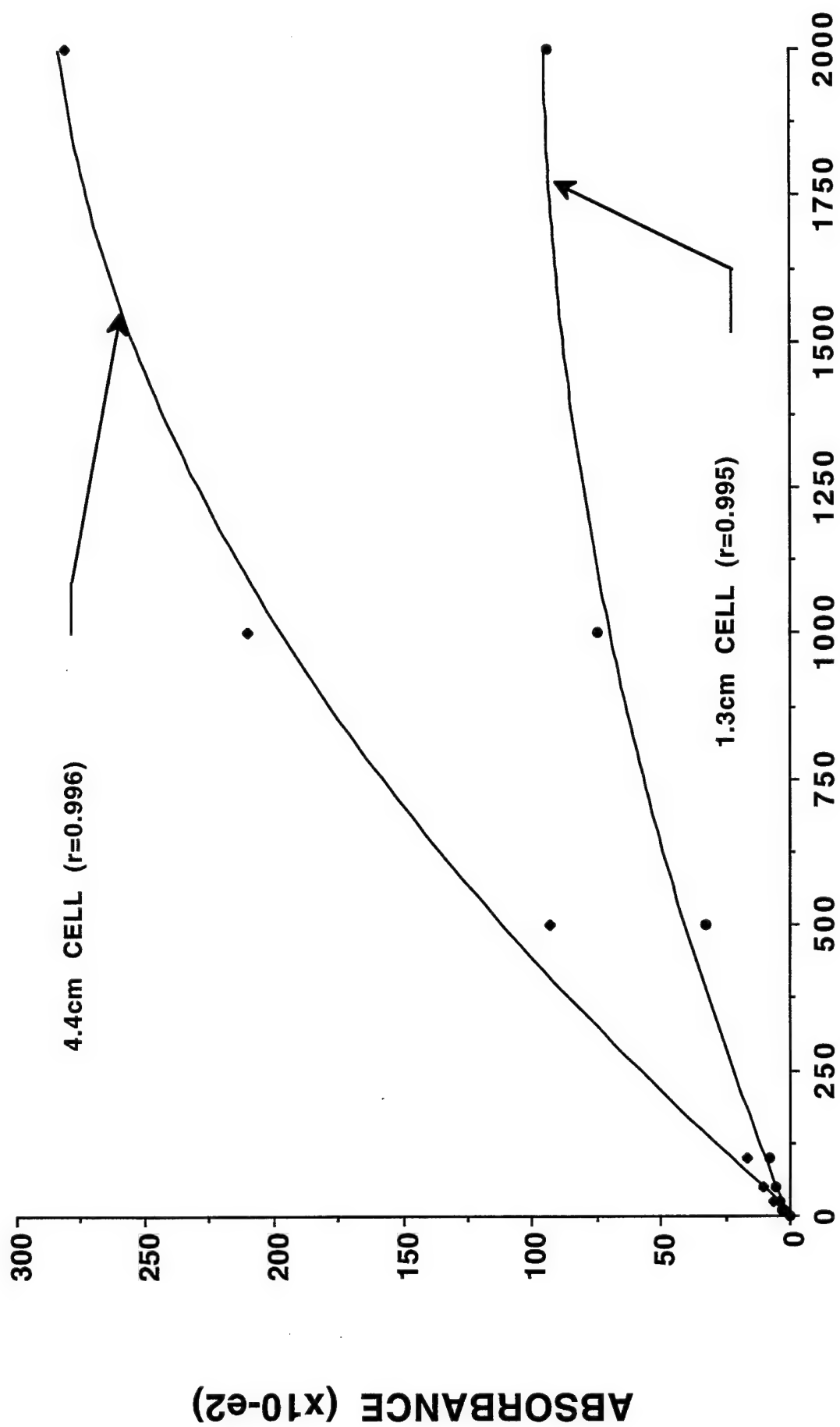


FIGURE 11 **Cu(I) CONCENTRATION (ppb)**

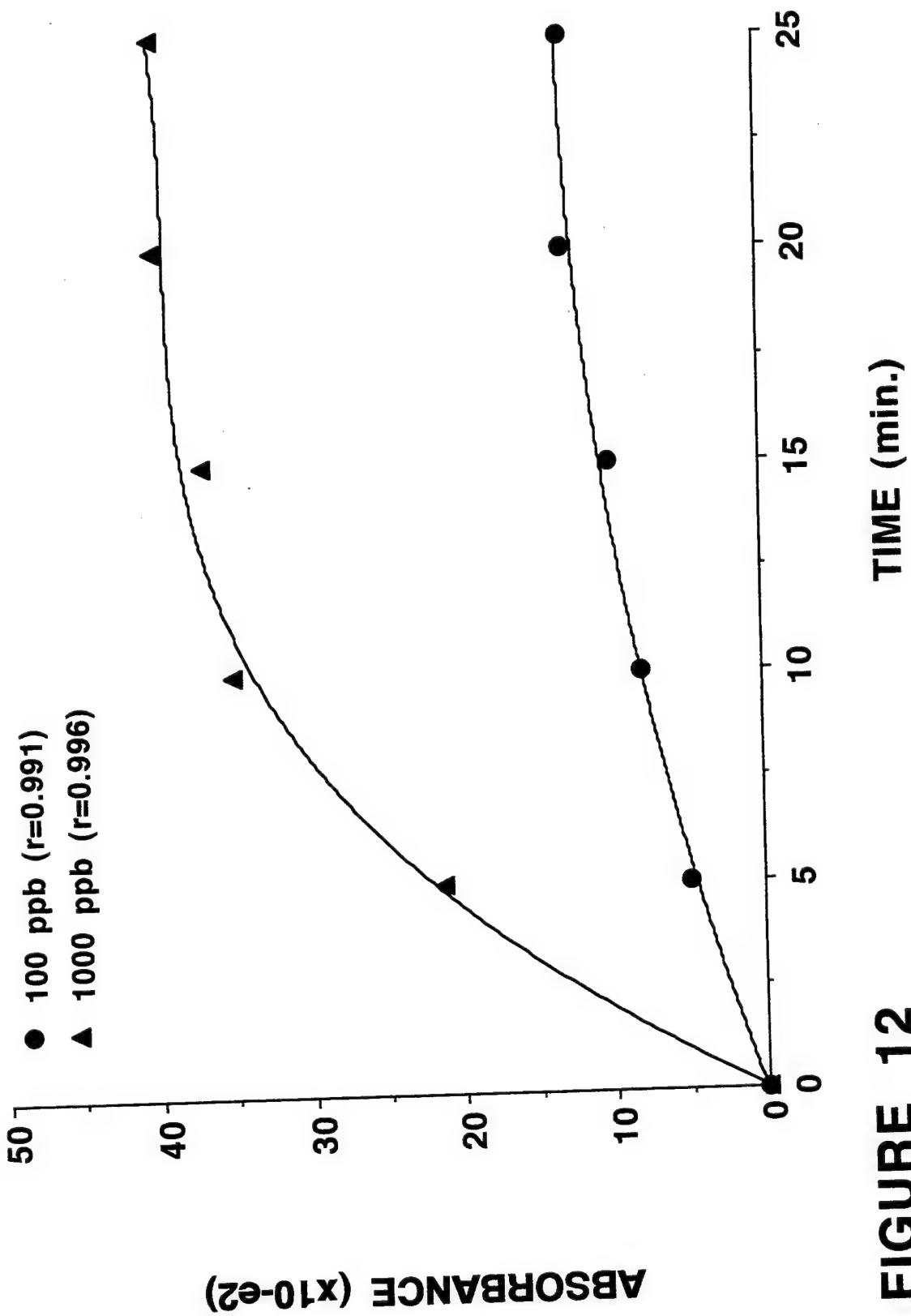


FIGURE 12

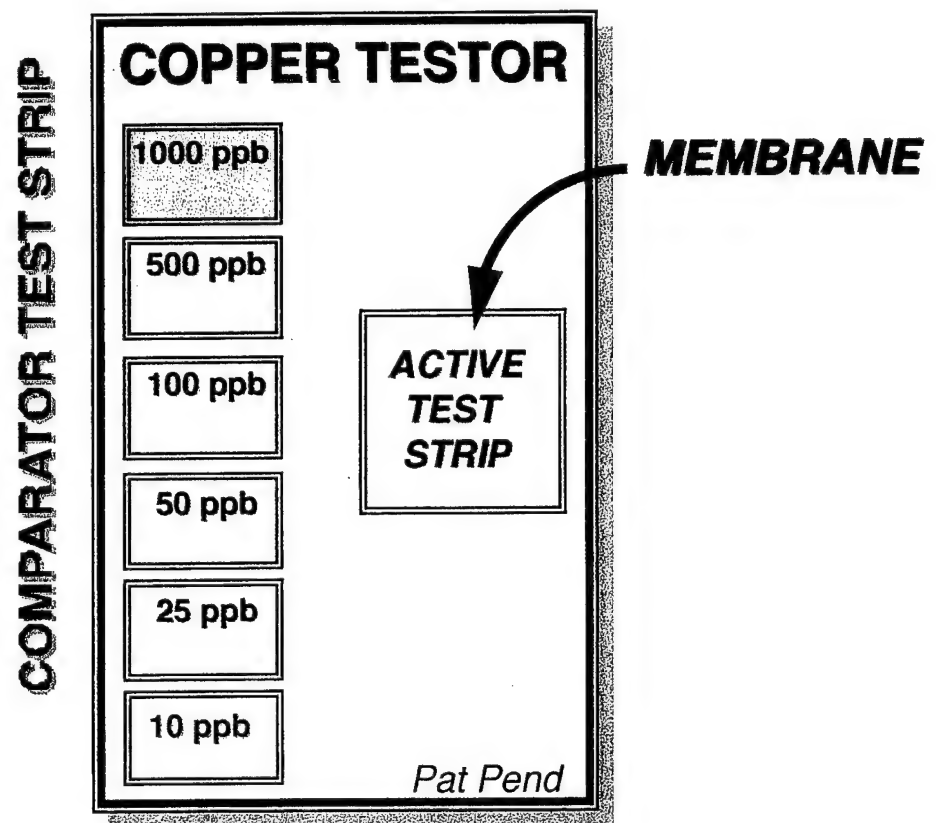
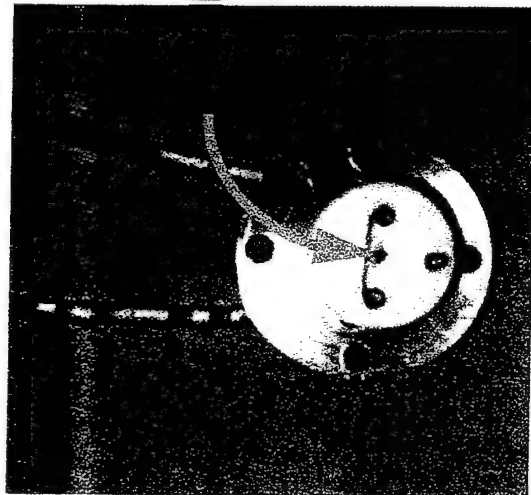
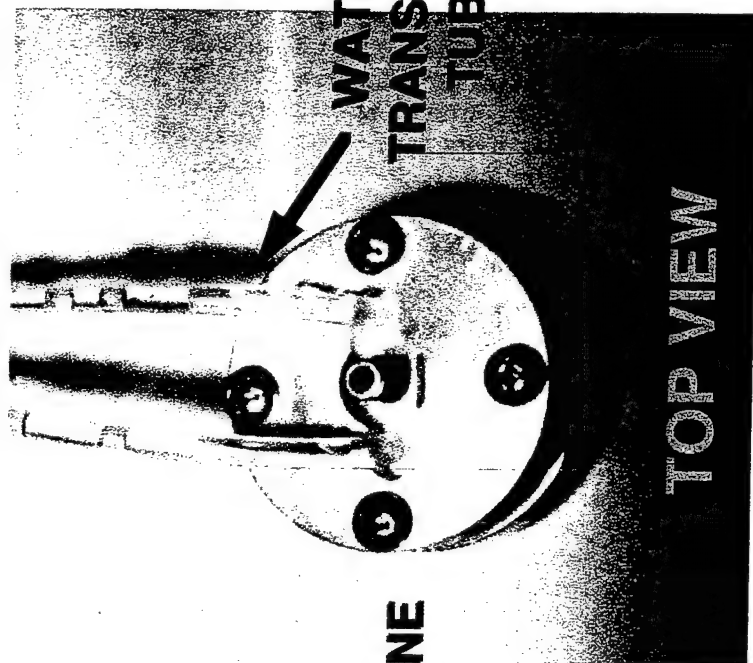


Figure 13.

**OPEN FLOW THROUGH
CELL W/ MEMBRANE**



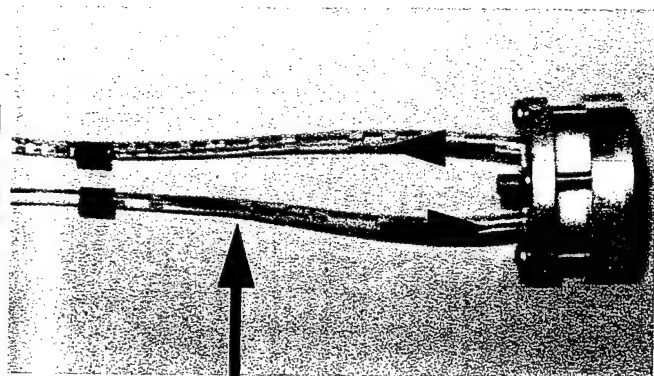
BRANE



**WATER
TRANSPORT
TUBES**

TOP VIEW

**FLOW THROUGH
CELL**



SIDE VIEW

DISASSEMBLED FLOW THROUGH CELL

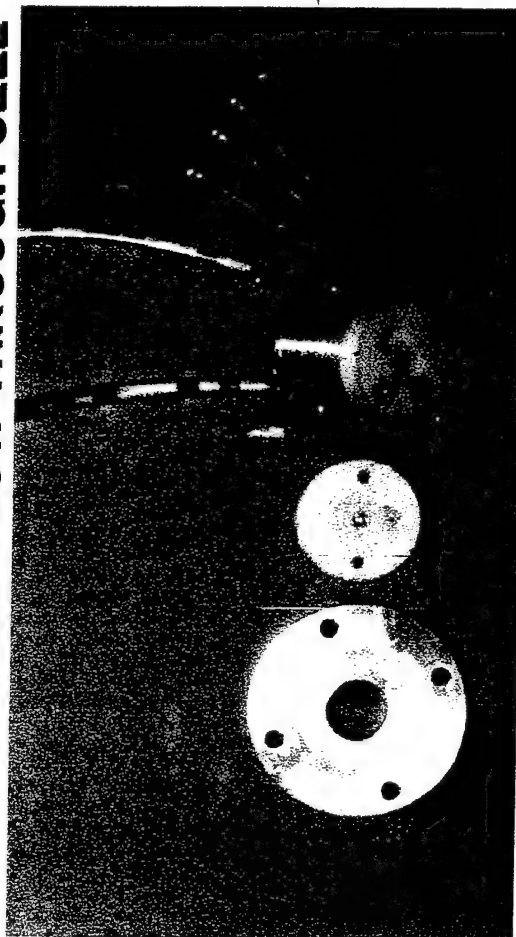


Figure 14.

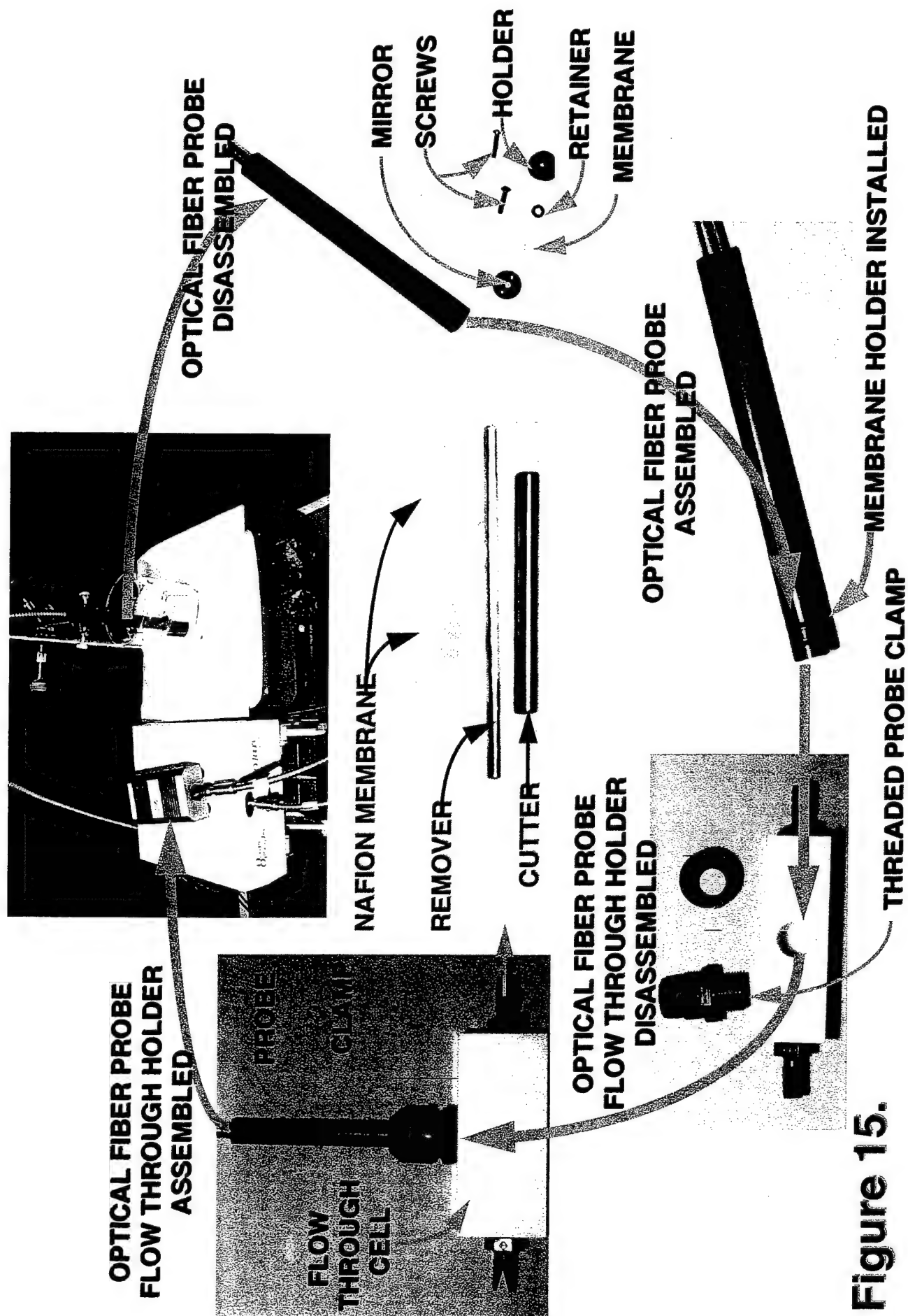


Figure 15.

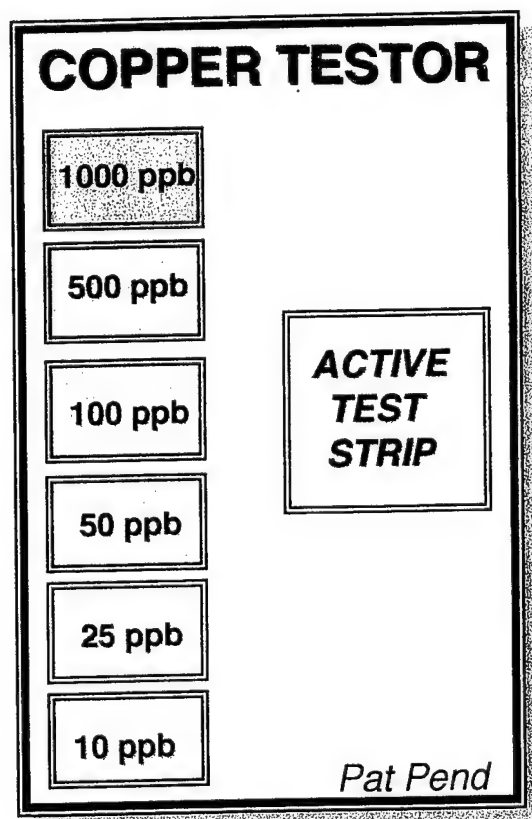
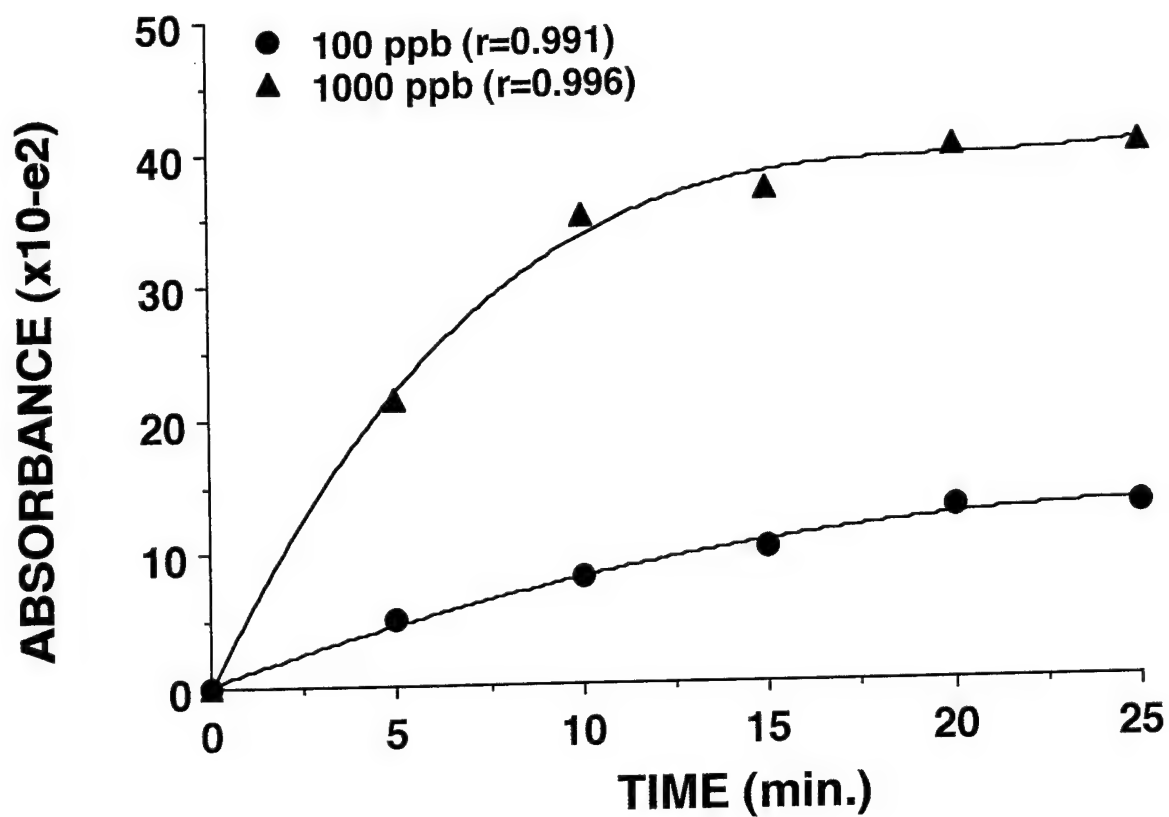


Figure 16.

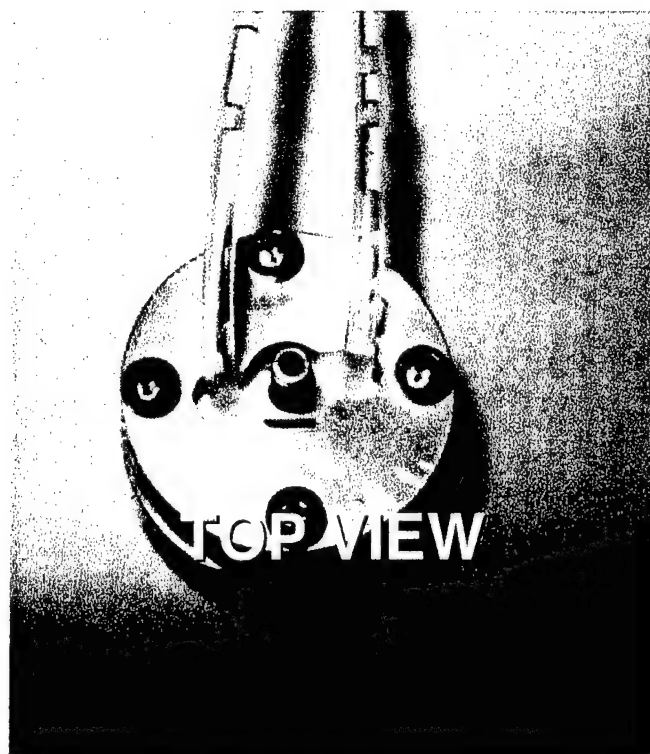
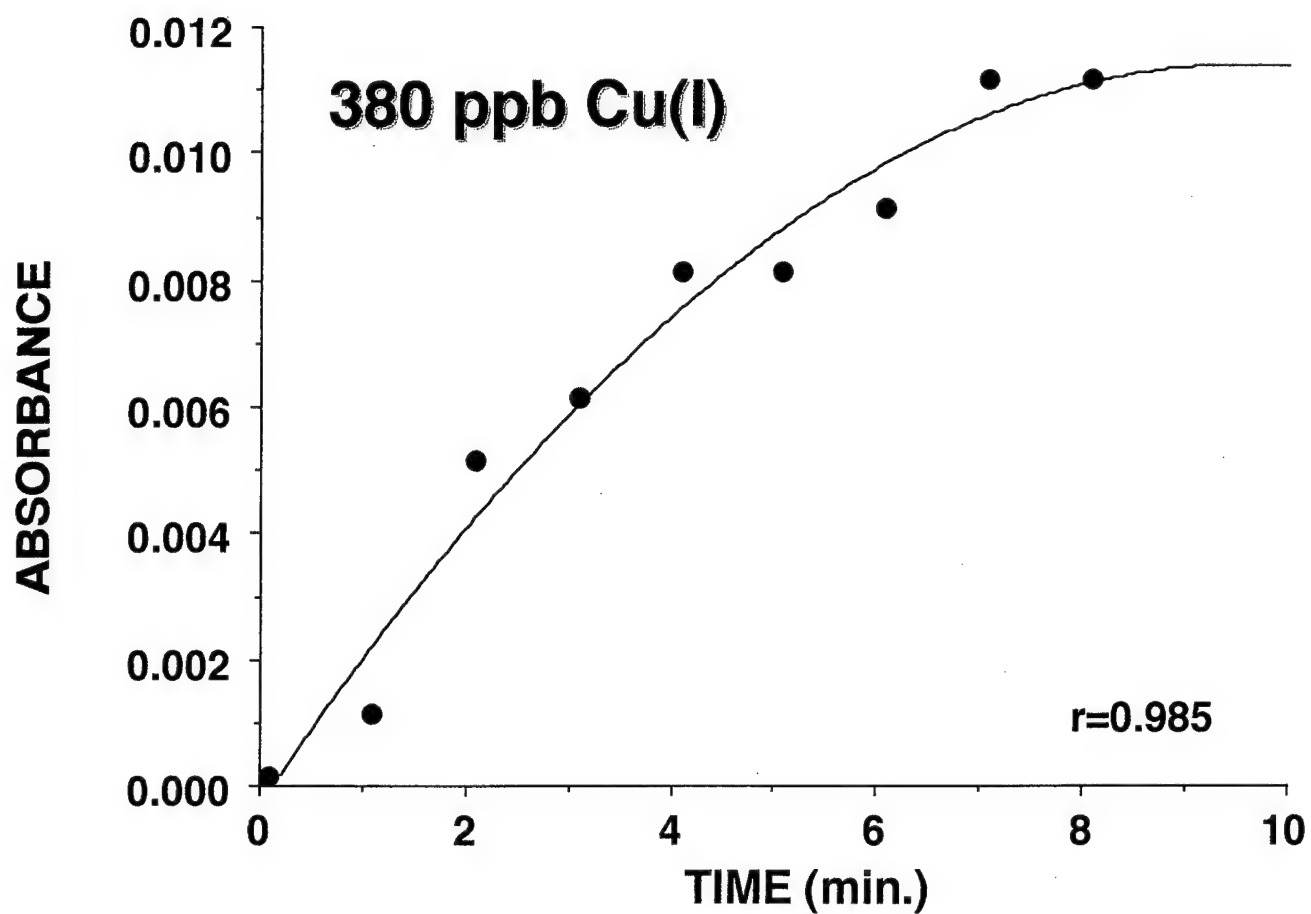


Figure 17.

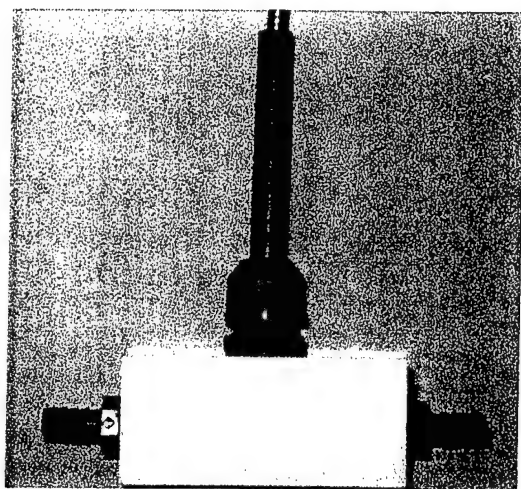
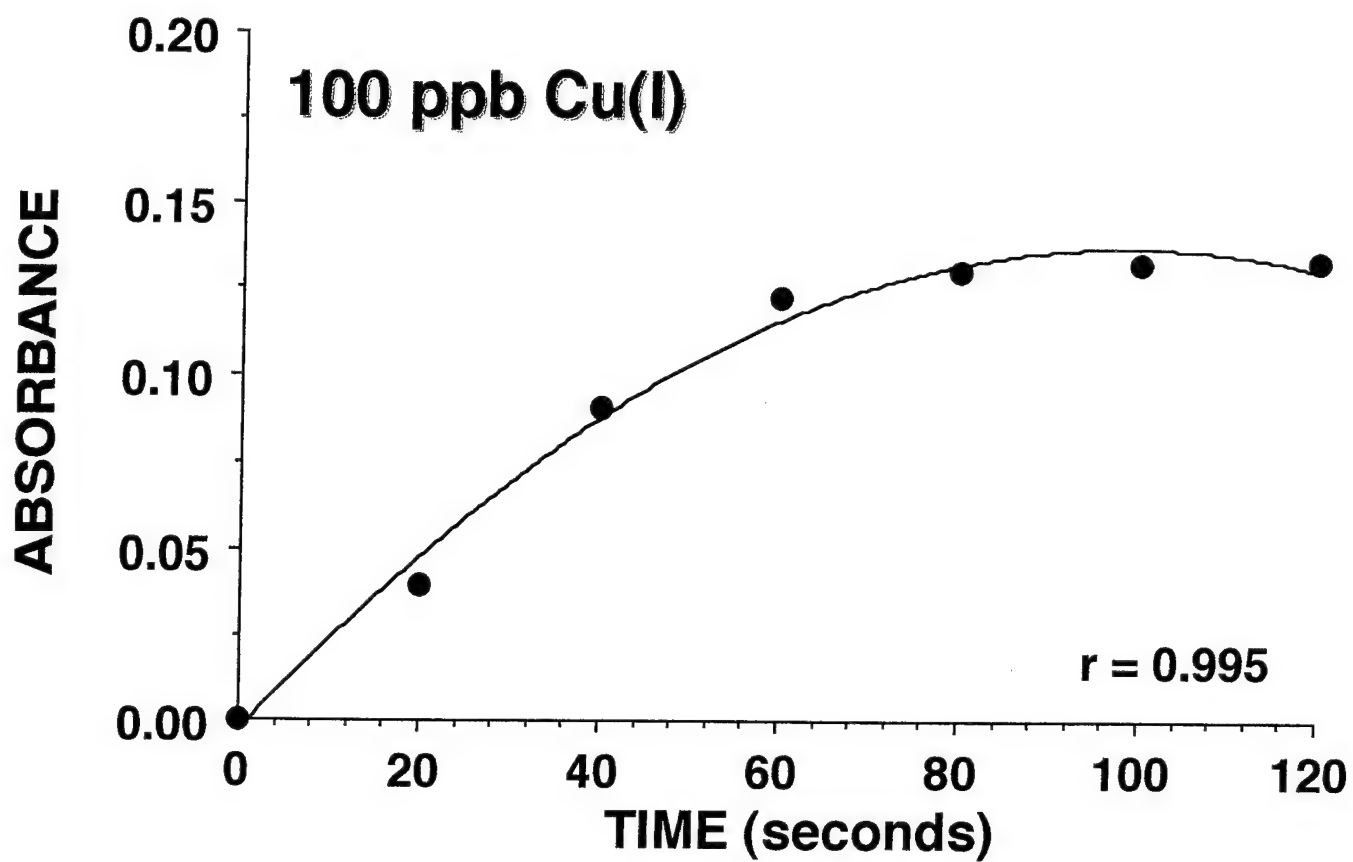
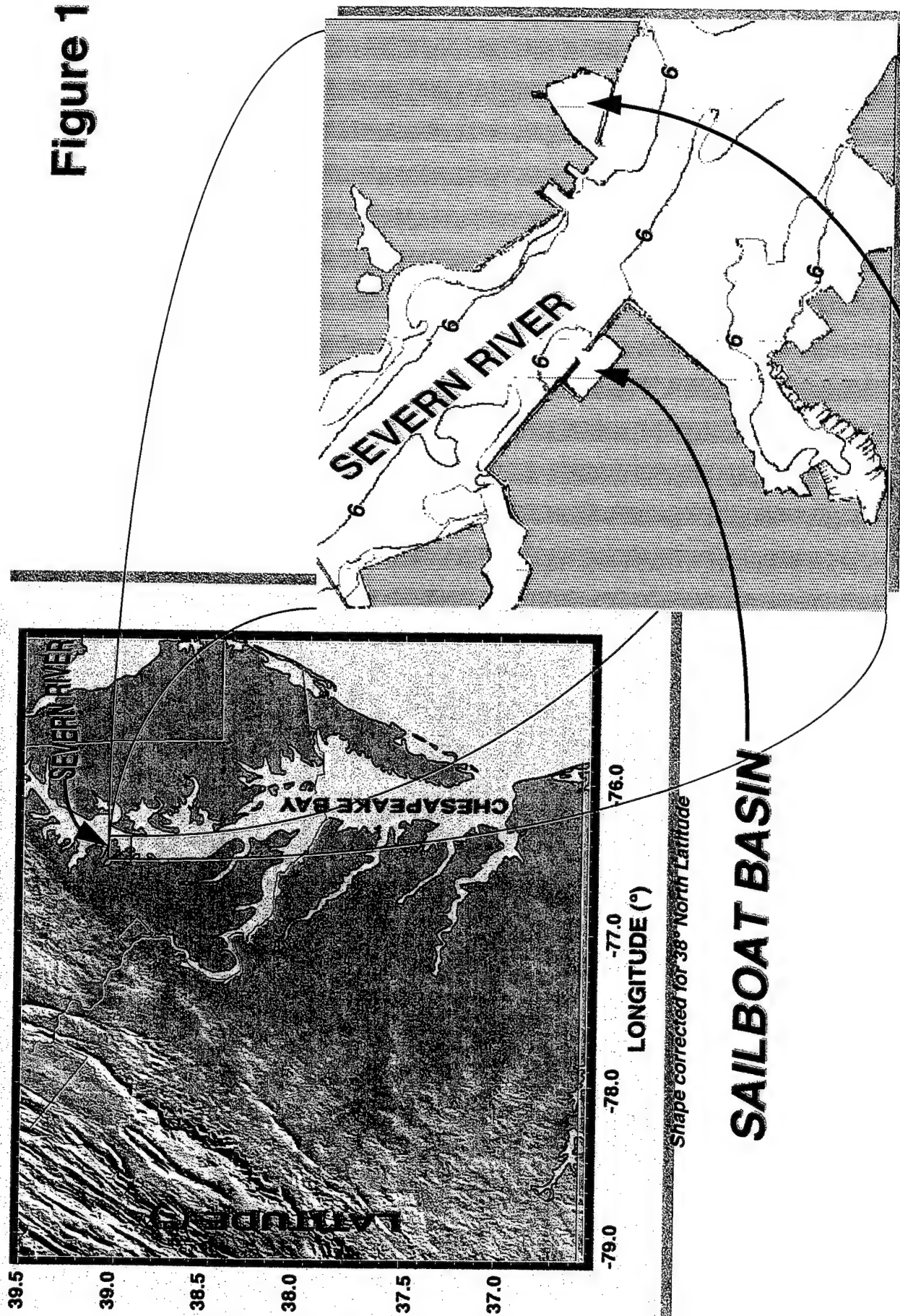


Figure 18.

Figure 19.



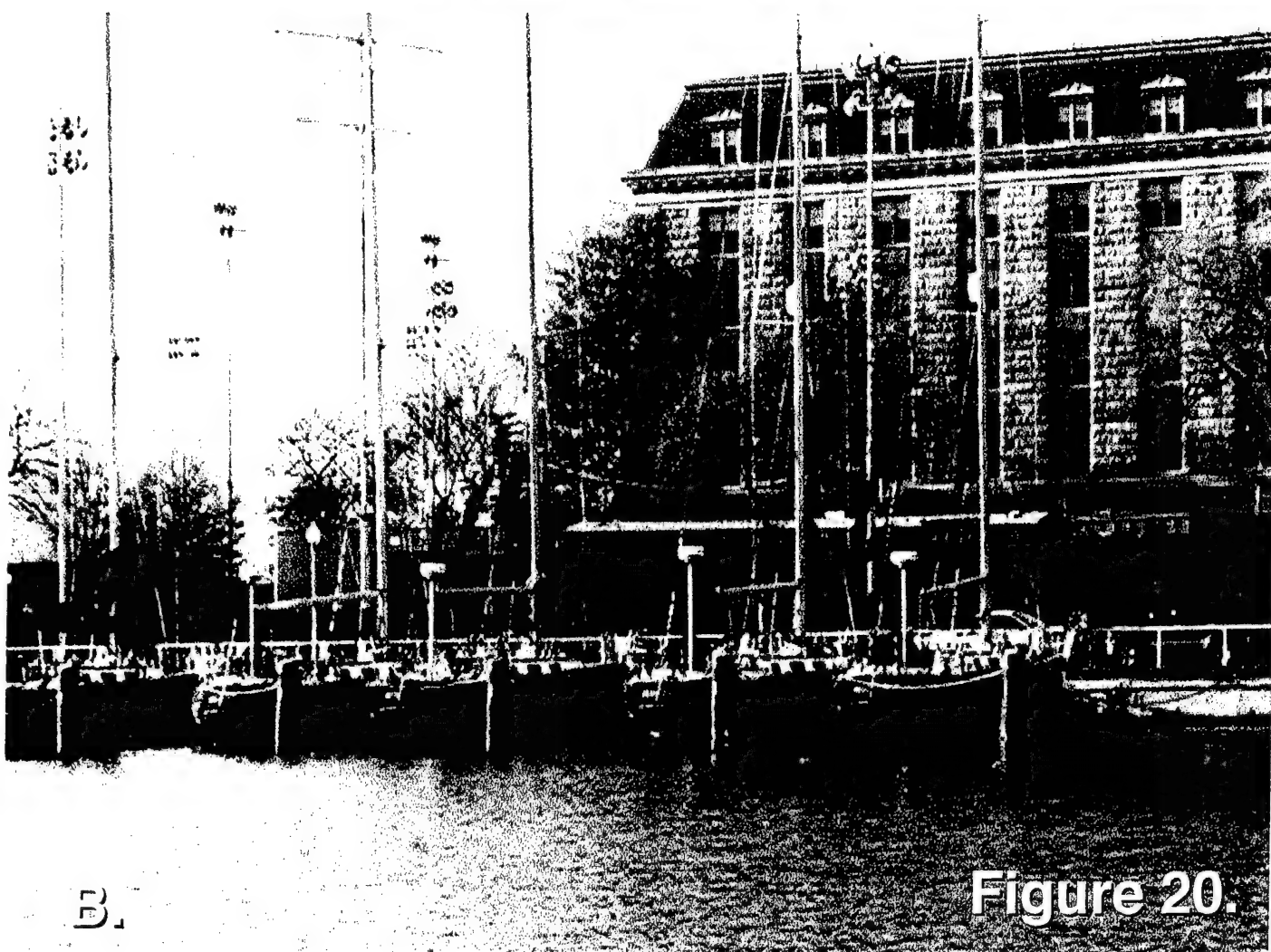


Figure 20.

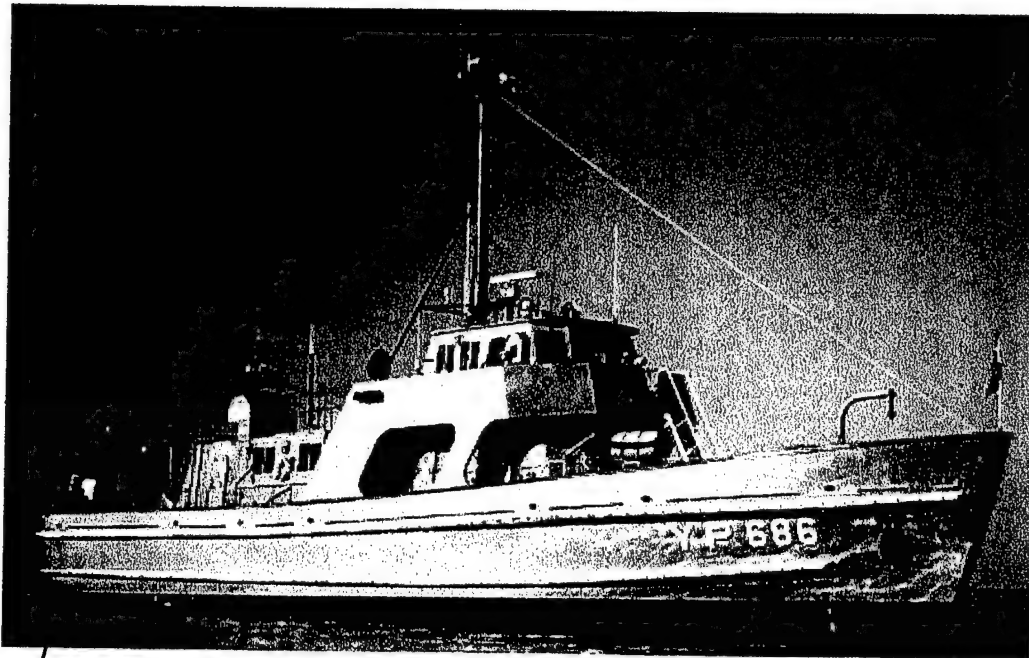


Figure 21.

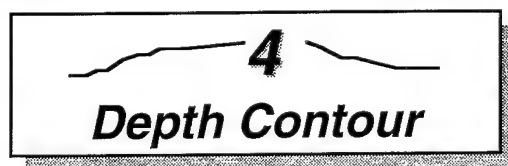
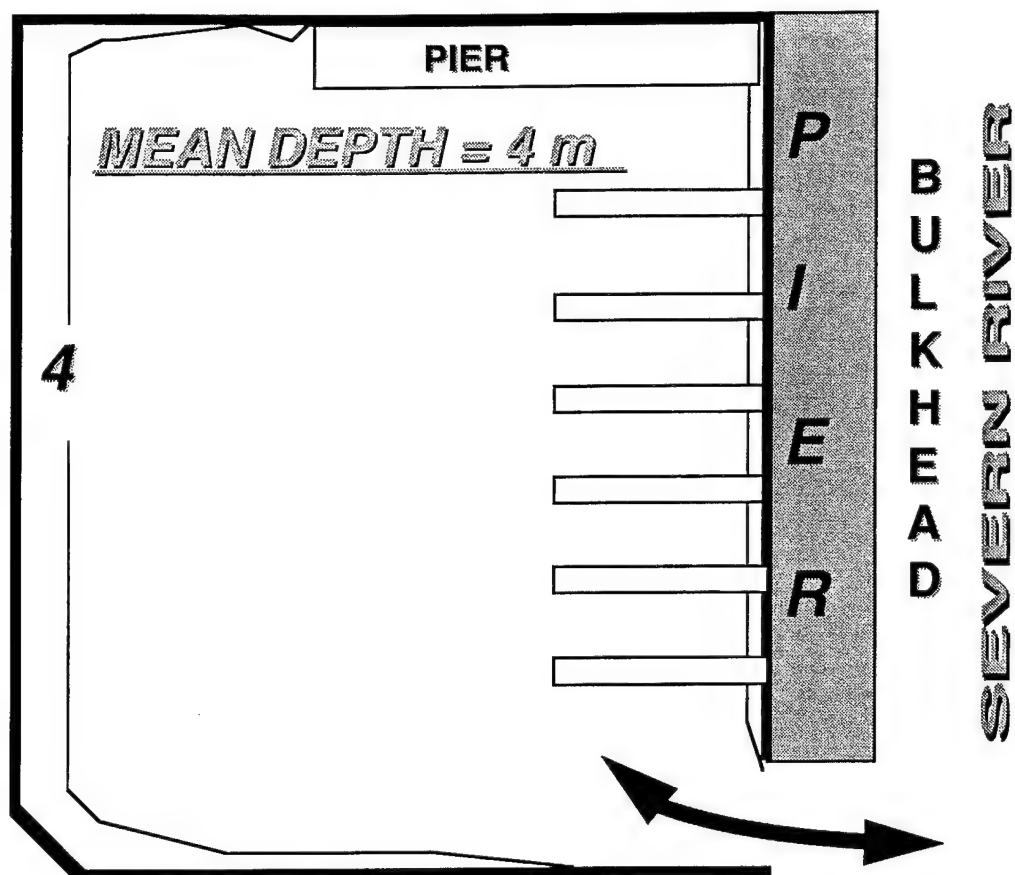
**YARD PATROL CRAFT
ANTIFOULING CHARACTERISTICS**

**COATING TYPE: LEACHING
-WOOLSEY NEPTUNE RED-**

**SURFACE LEACHING AREA:
361sq.m**

**ESTIMATED HOURLY RELEASE
OF COPPER (I):
1.1 - 1.5ppb/sq.cm/hr**

A.



B.

Figure 22.

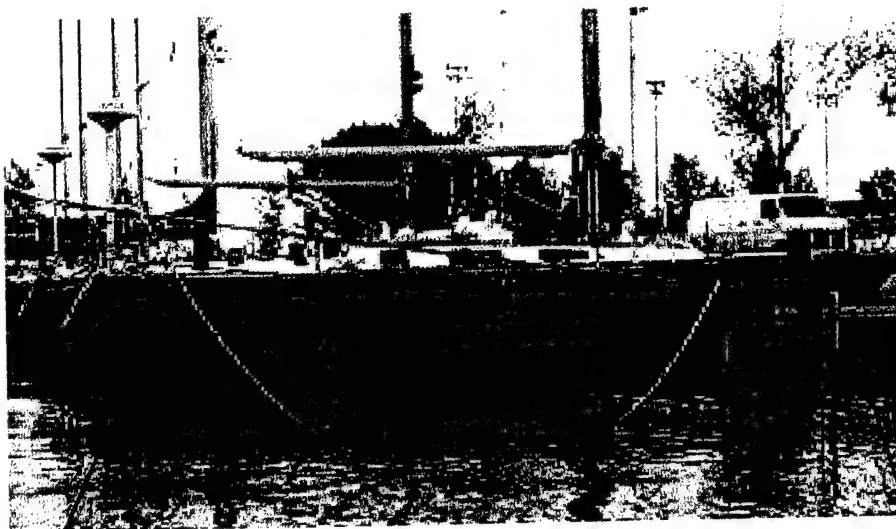


Figure 23.

**SAILBOAT
ANTIFOULING CHARACTERISTICS**

**COATING TYPE: LEACHING
-WOOLSEY NEPTUNE RED-**

**SURFACE LEACHING AREA:
139 sq.m**

**ESTIMATED HOURLY RELEASE
OF COPPER (I):
1.1 - 1.5ppb/sq.cm/hr**

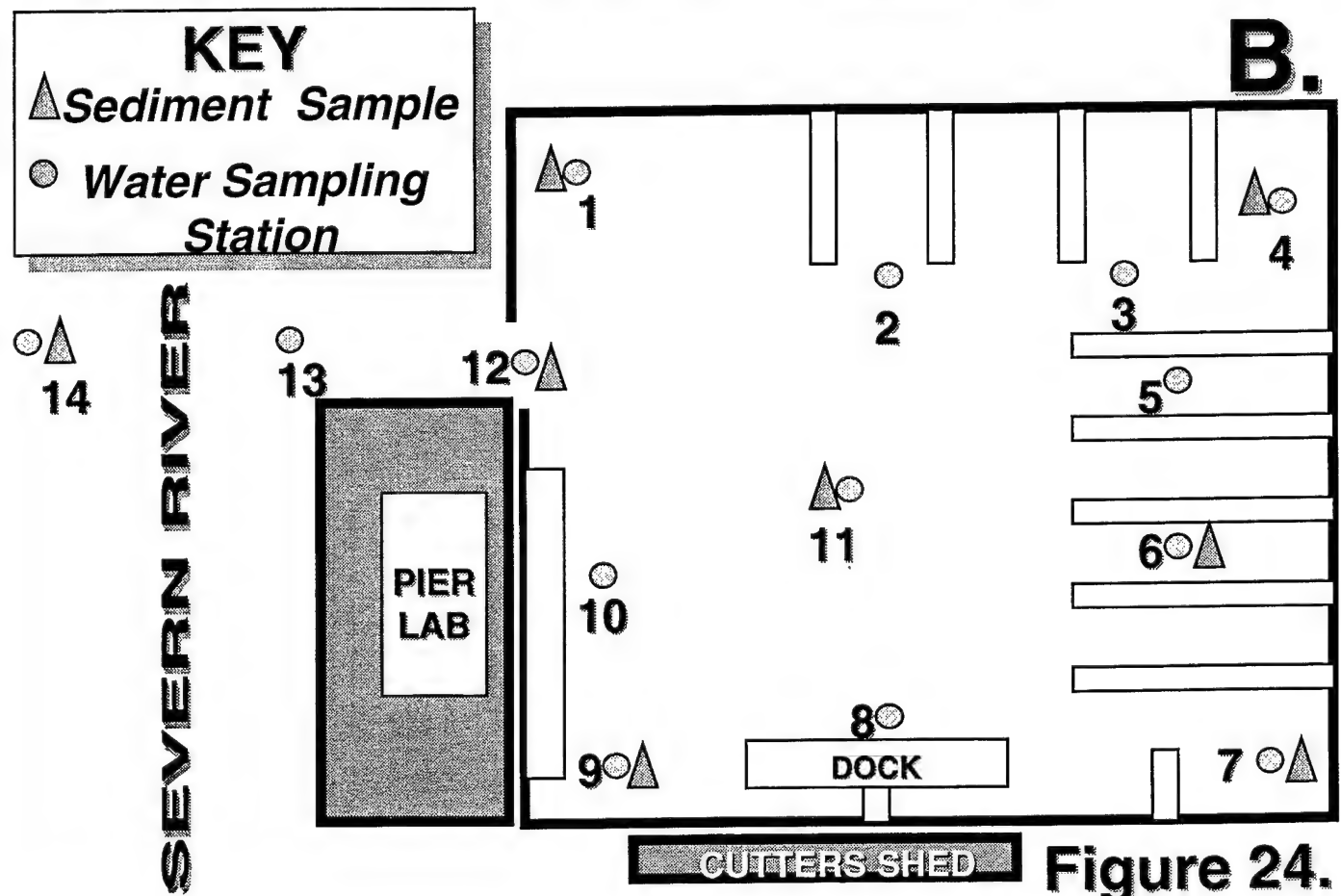
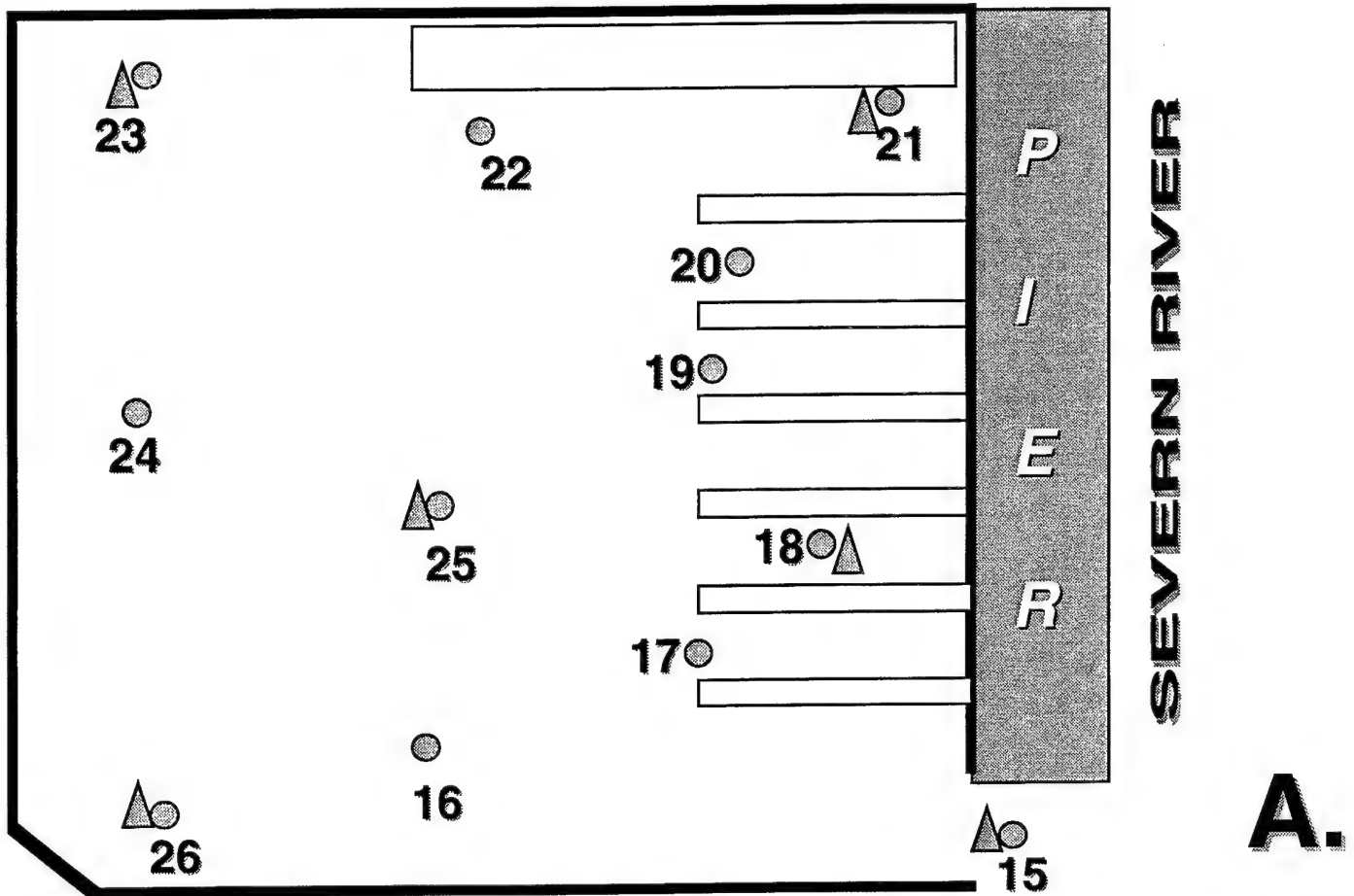


Figure 24.

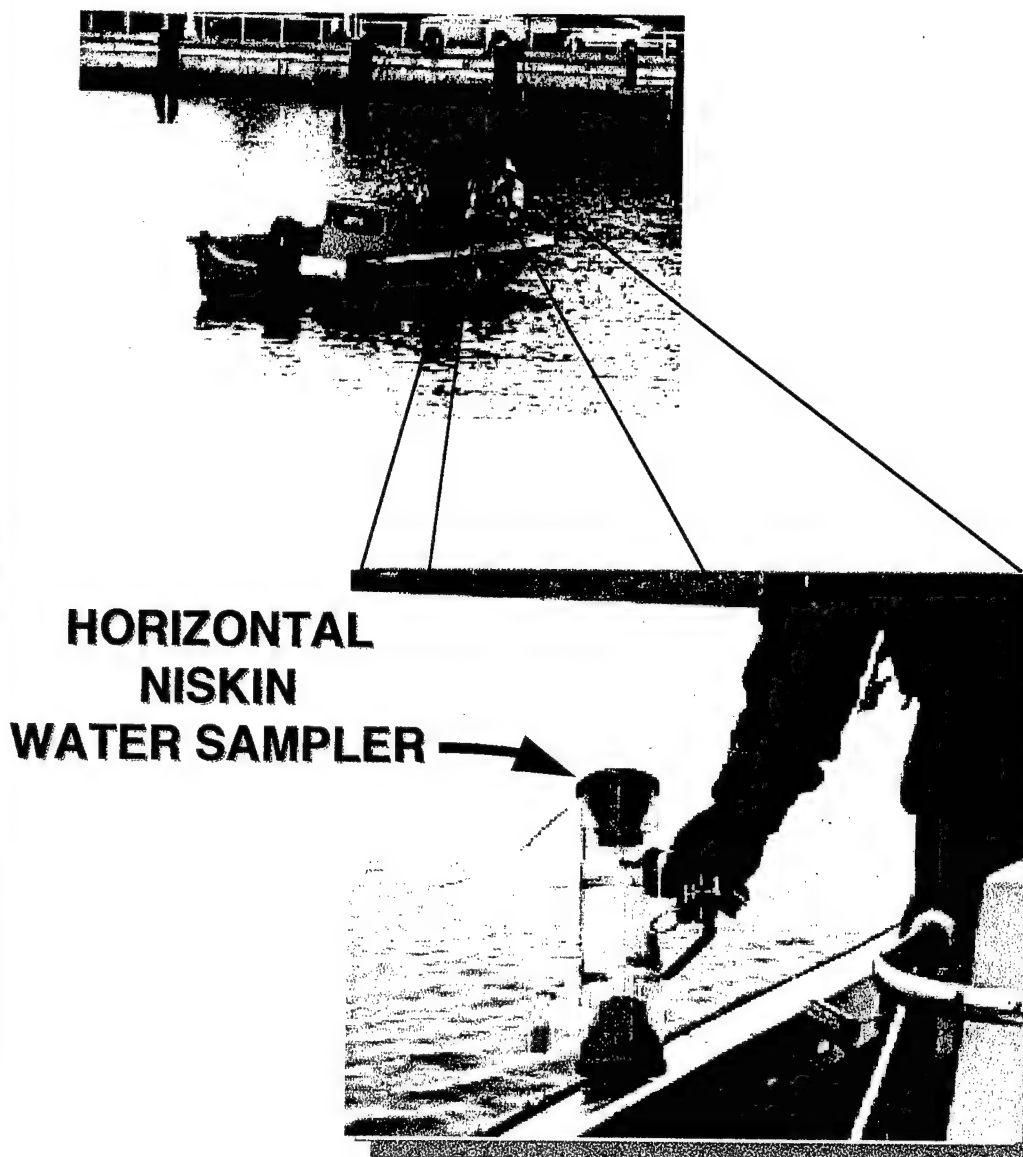
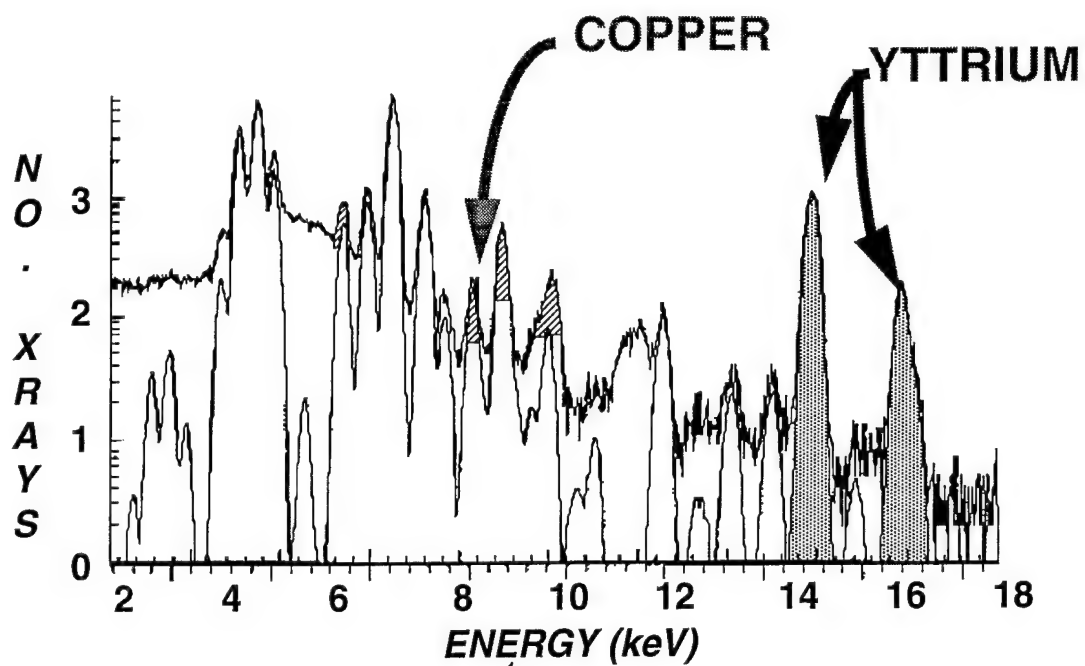


Figure 25.

A.



B.

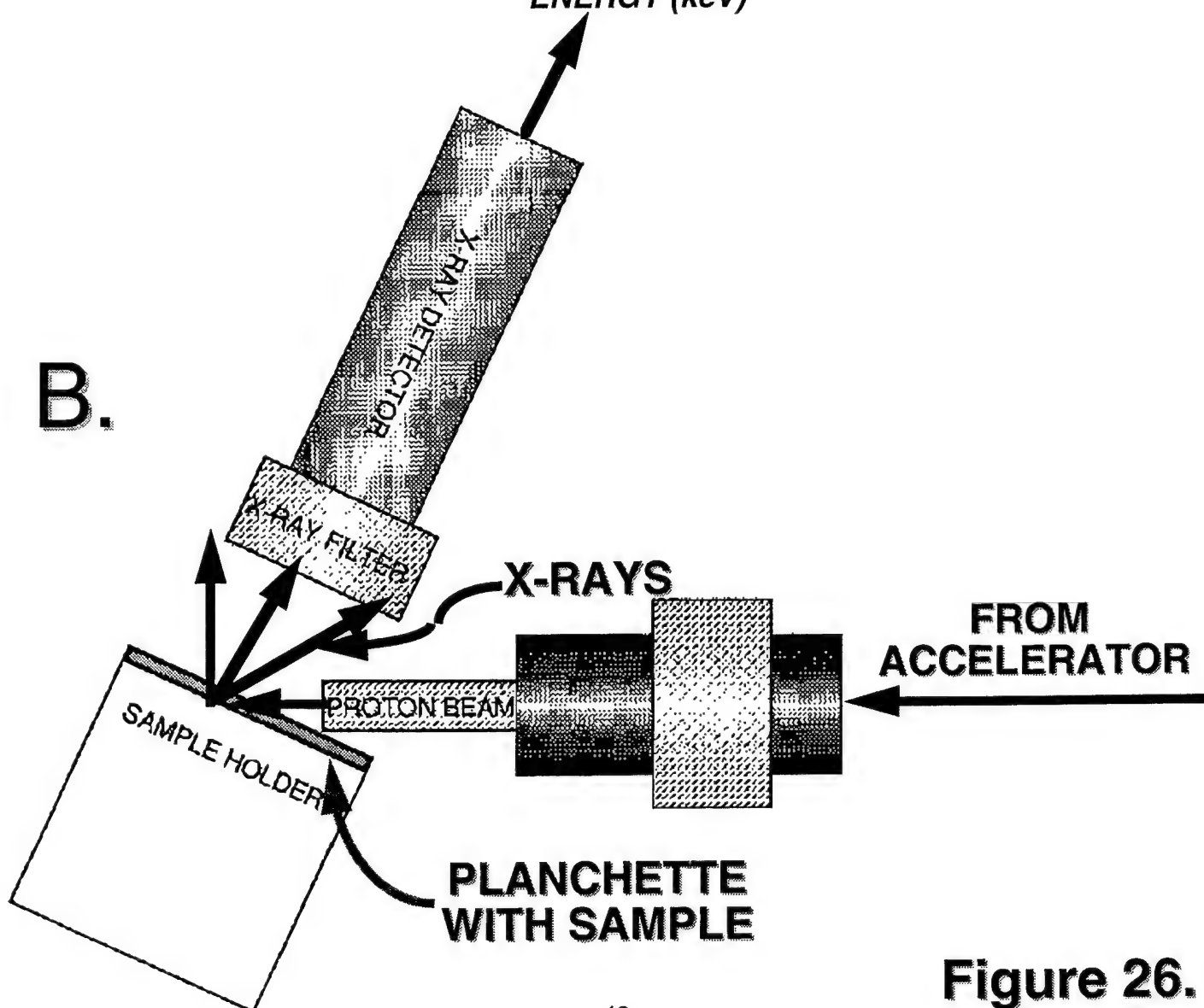


Figure 26.

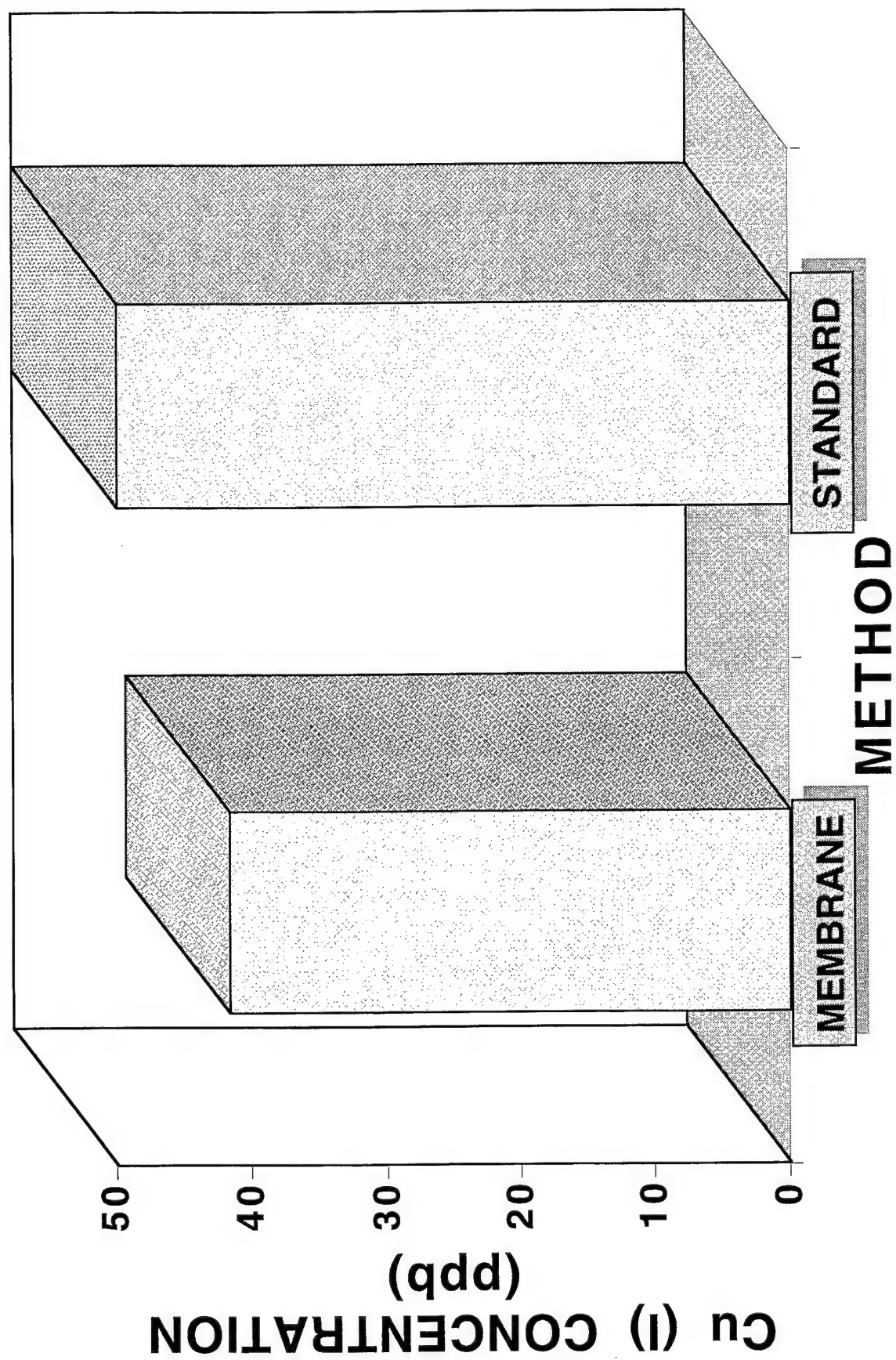


Figure 27.

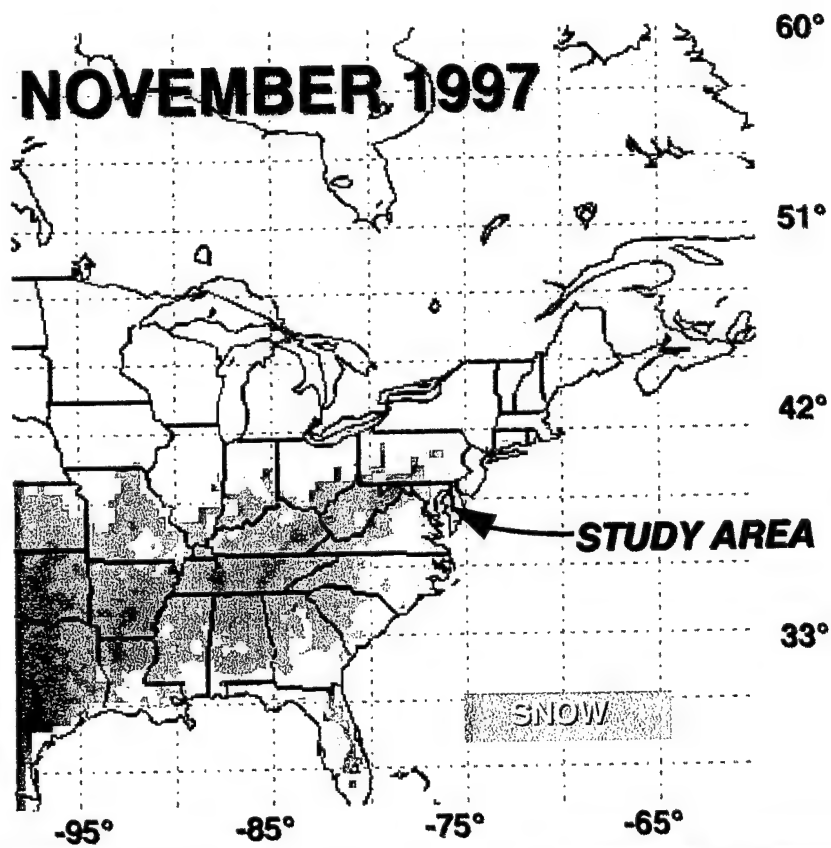
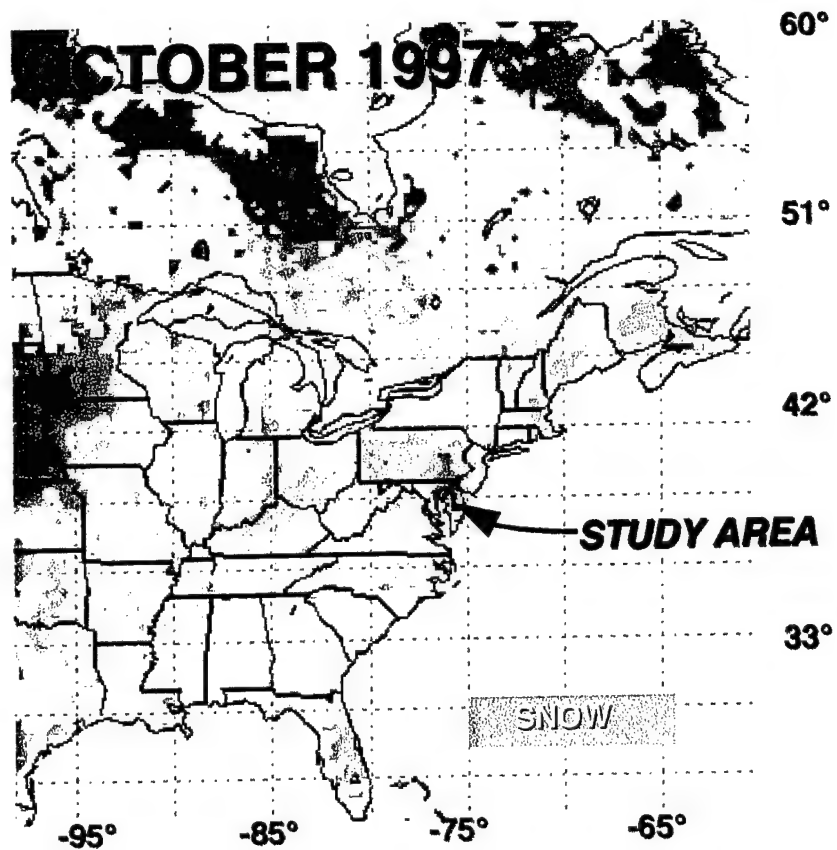
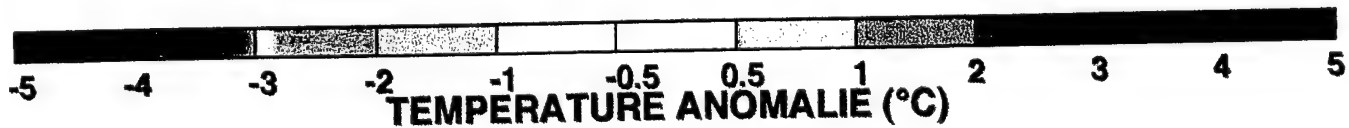


Figure 28.



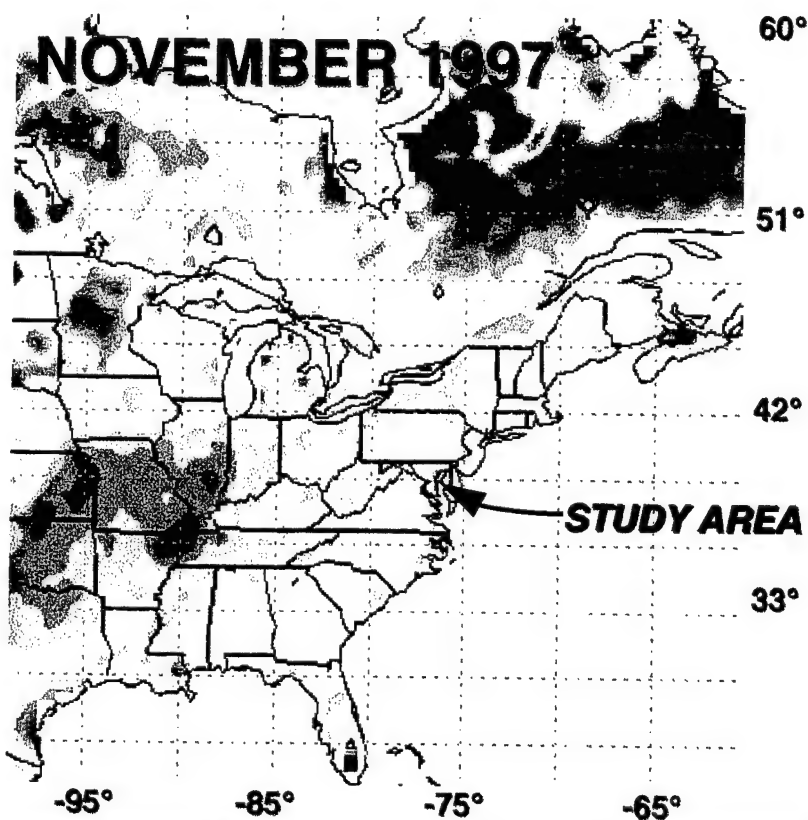
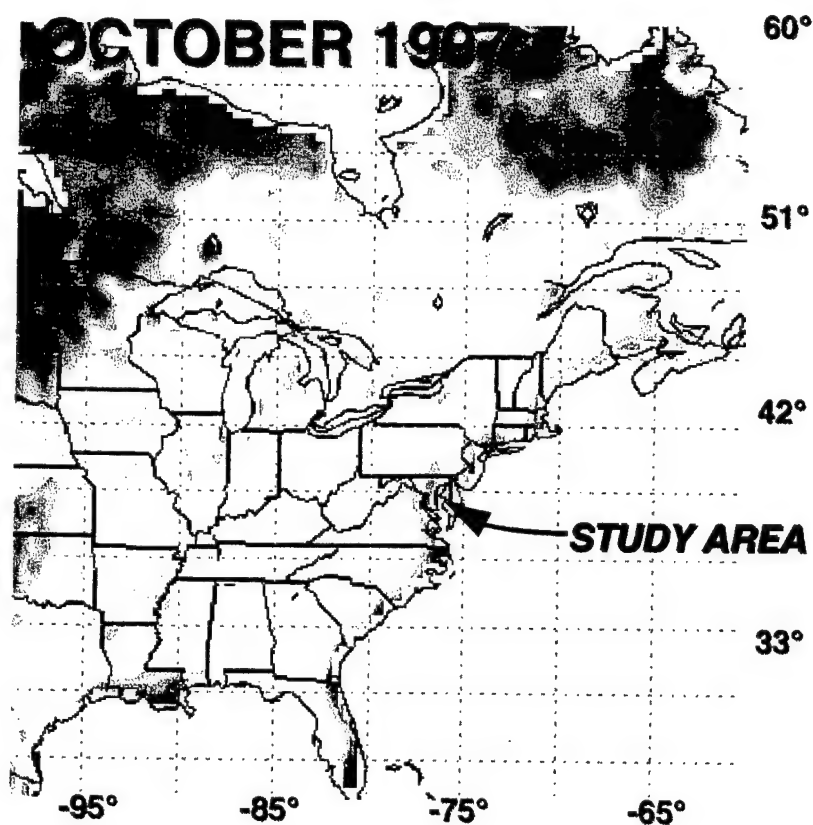
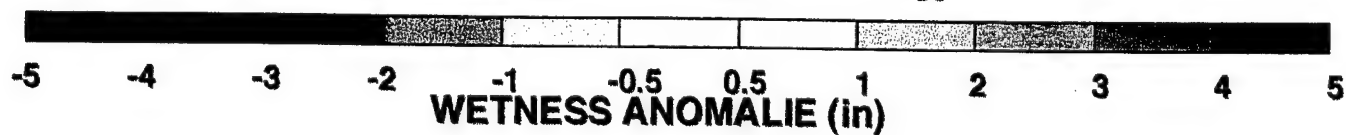


Figure 29.



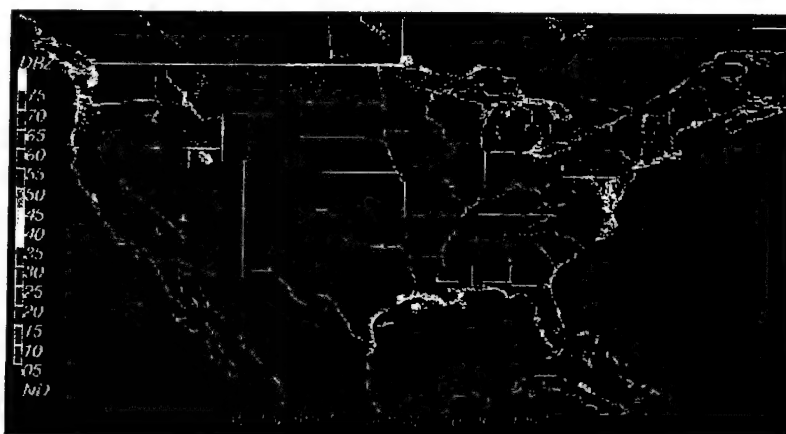
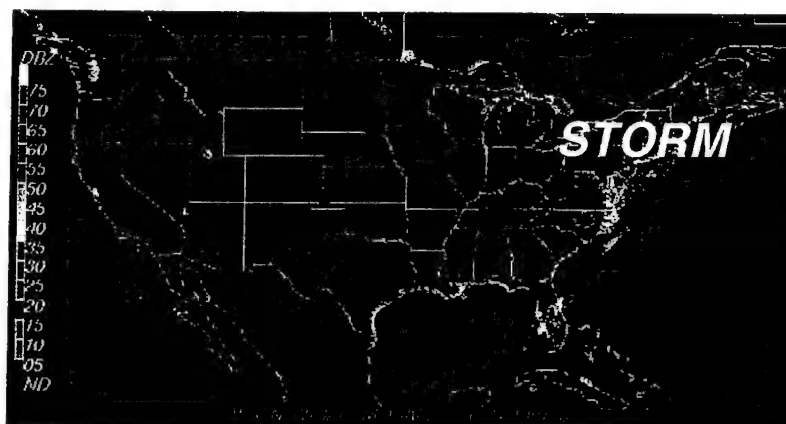
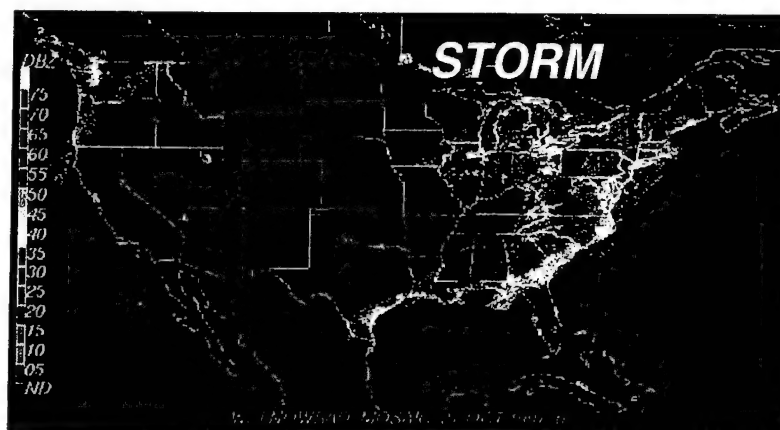


Figure 30.

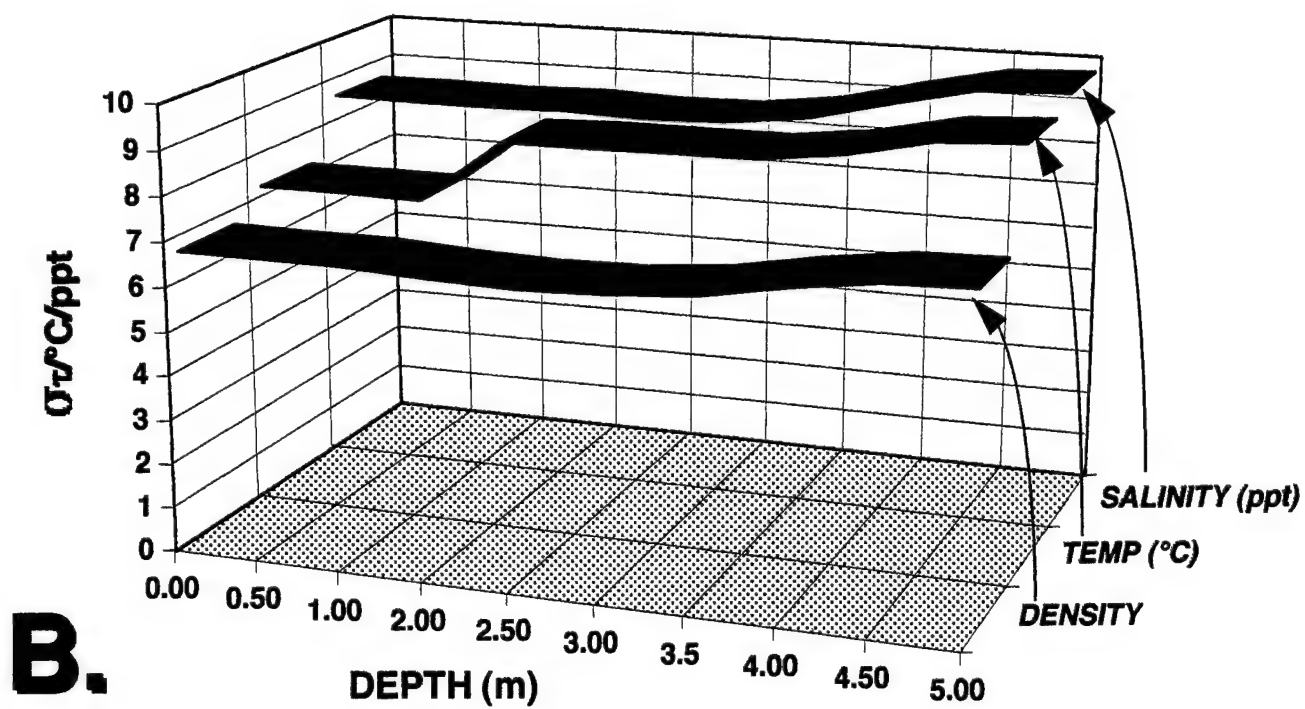
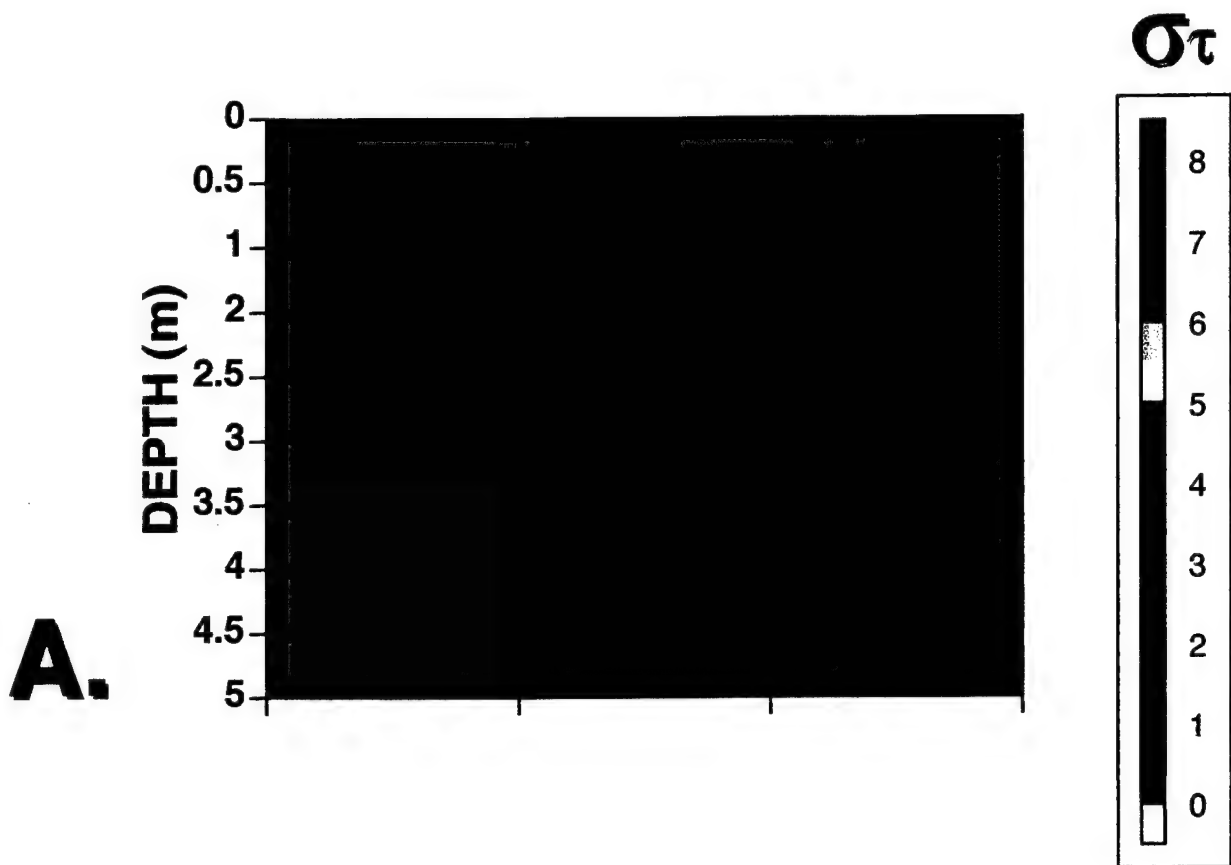


Figure 31.

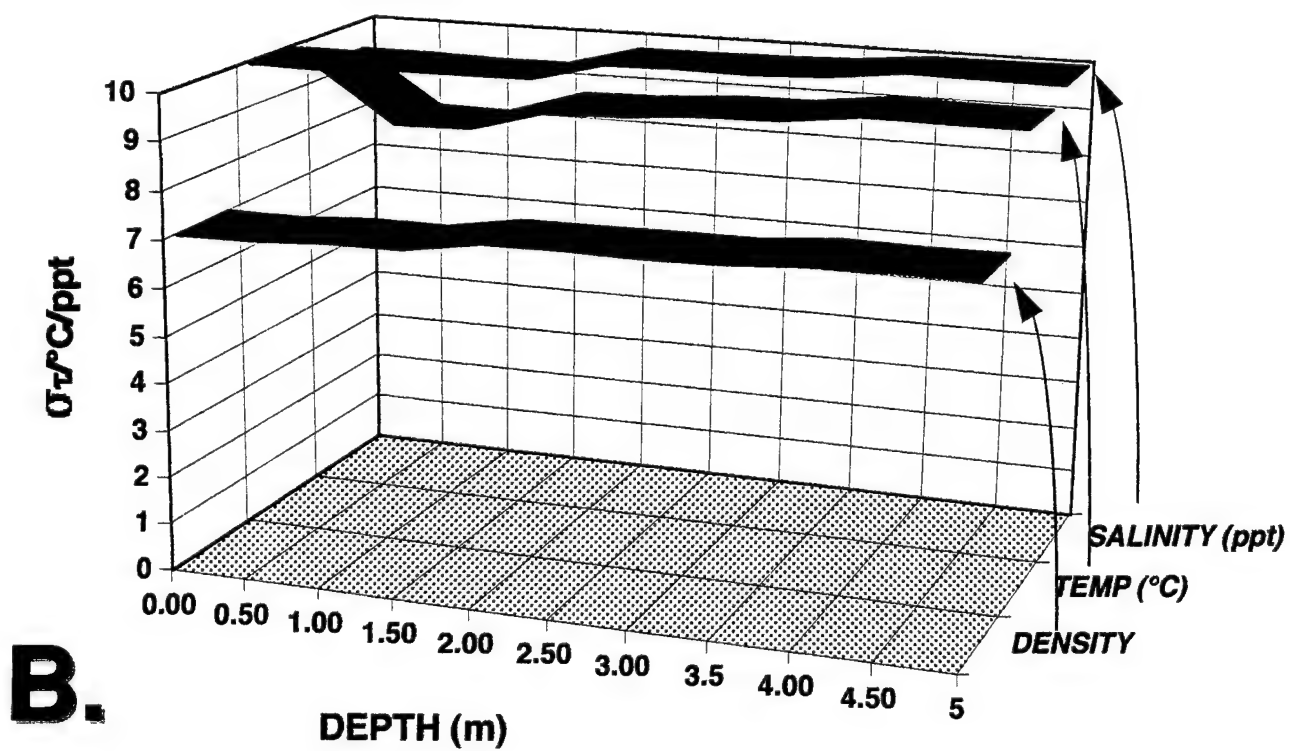
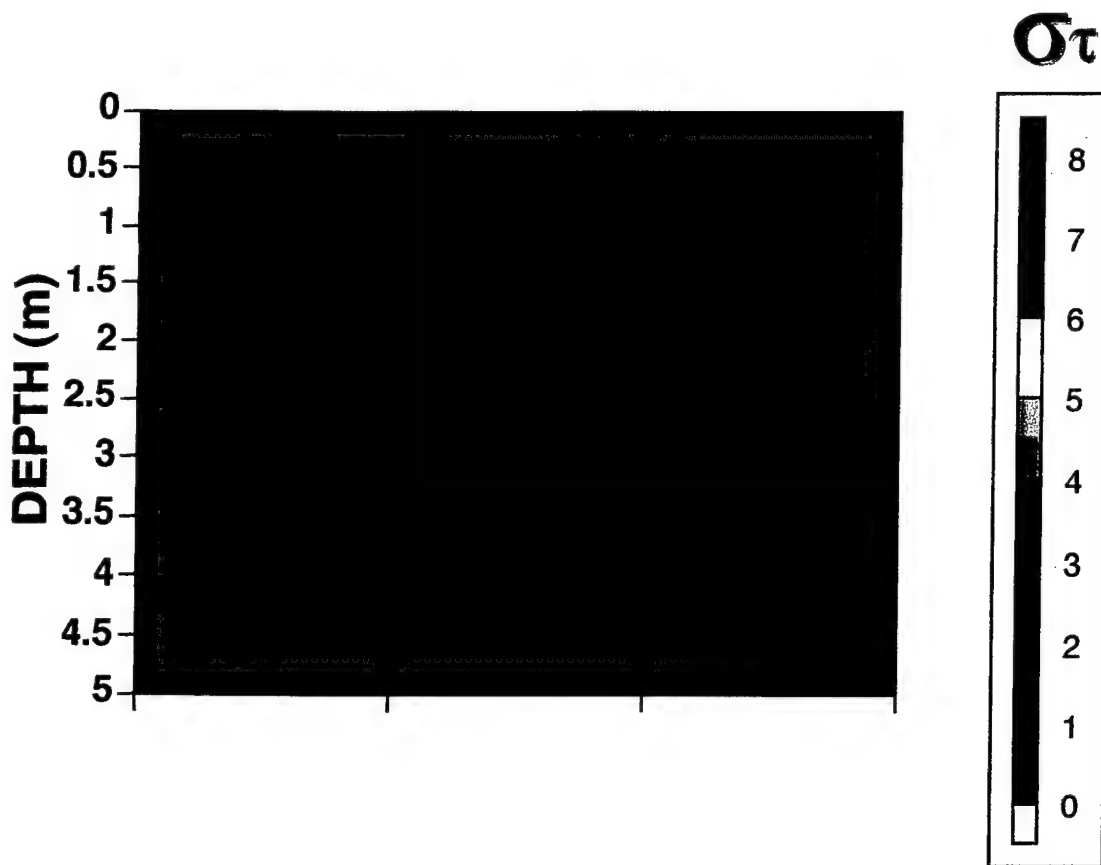


Figure 32.

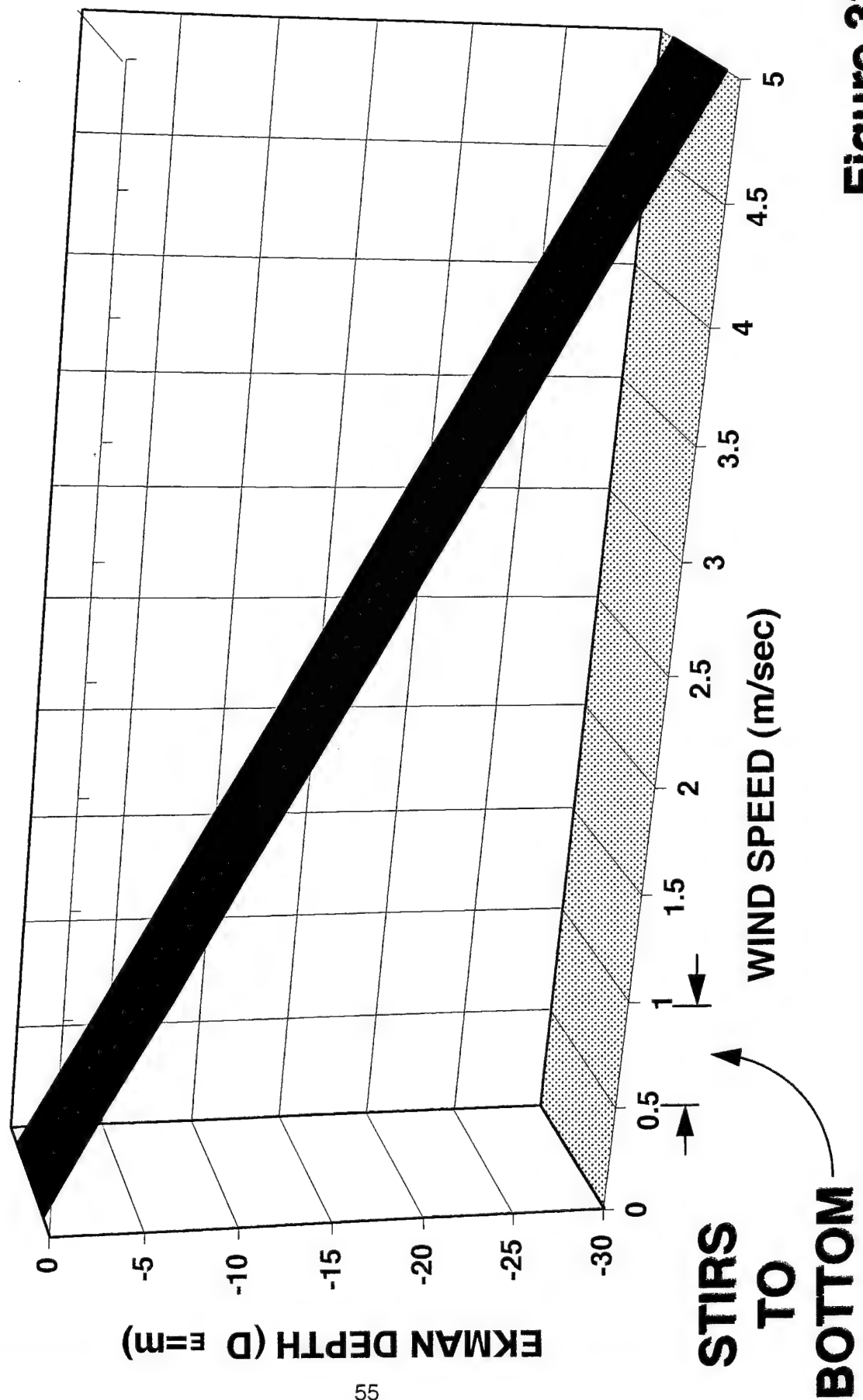
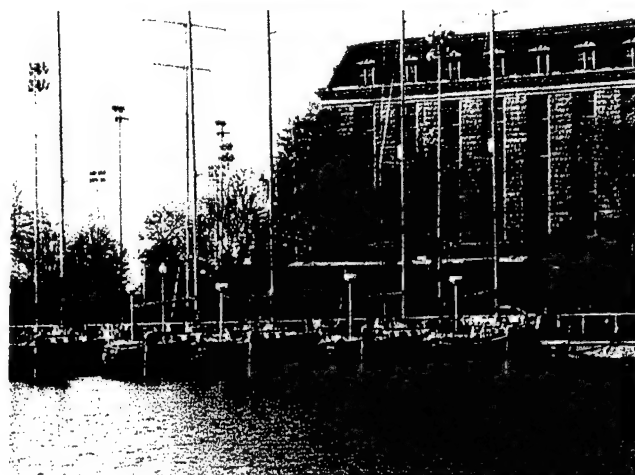
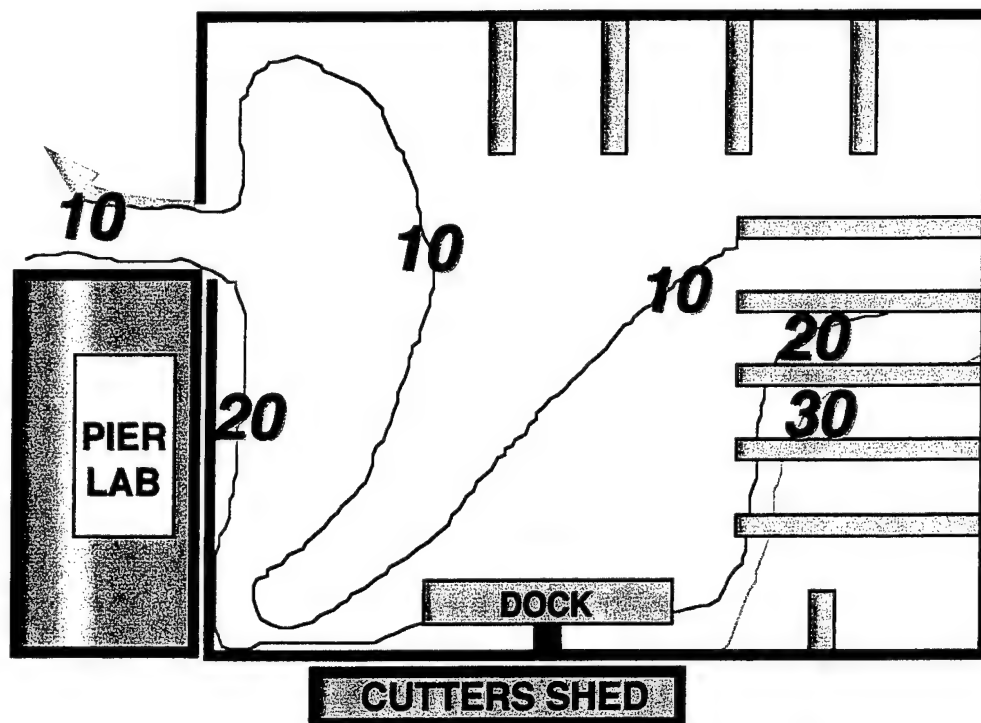


Figure 33.



SANTEE BASIN

MEAN DEPTH = 3 m

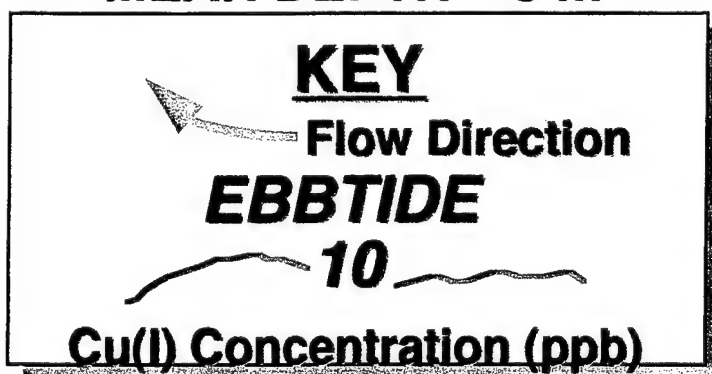
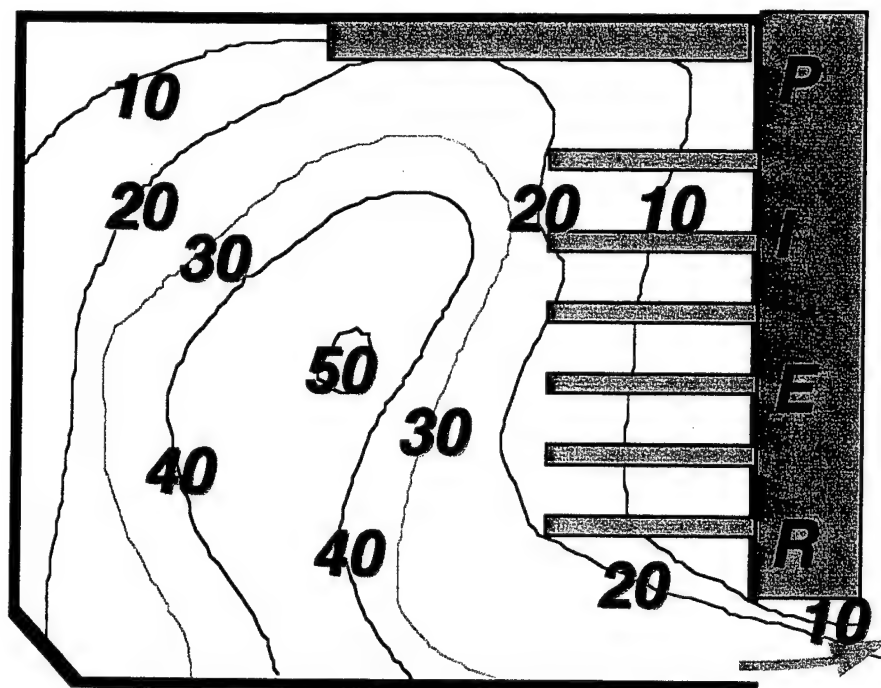


Figure 34.



NAVY ANNAPOLIS HARBOR YARD PATROL CRAFT BASIN

MEAN DEPTH = 4 m

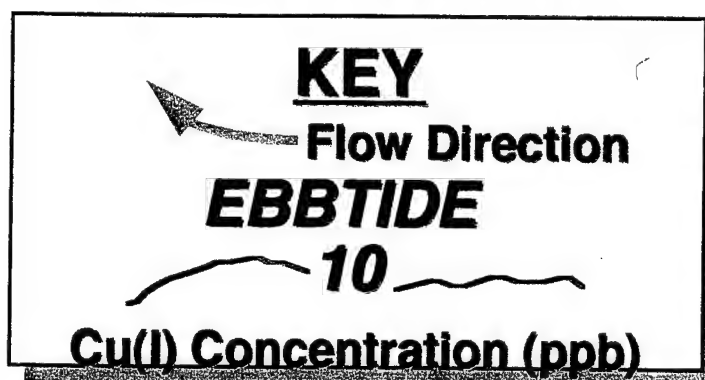


Figure 35.

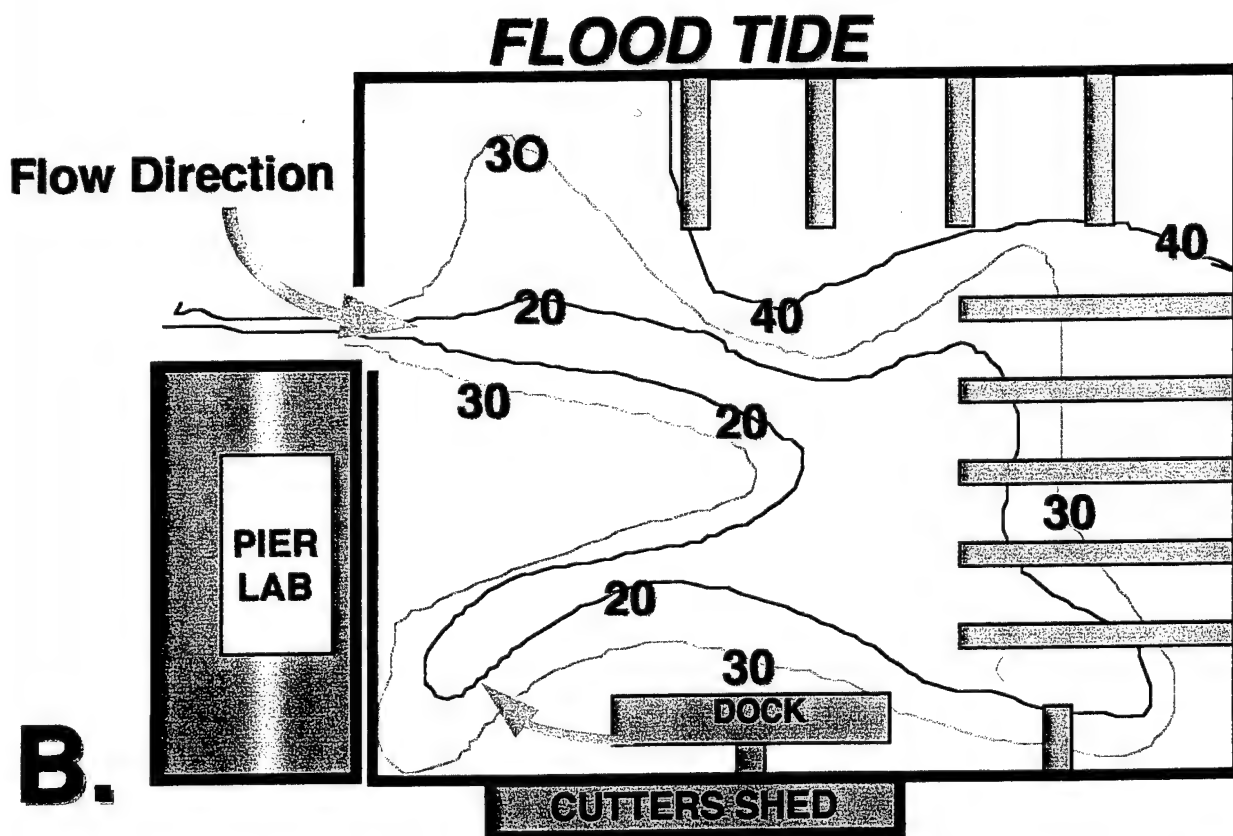
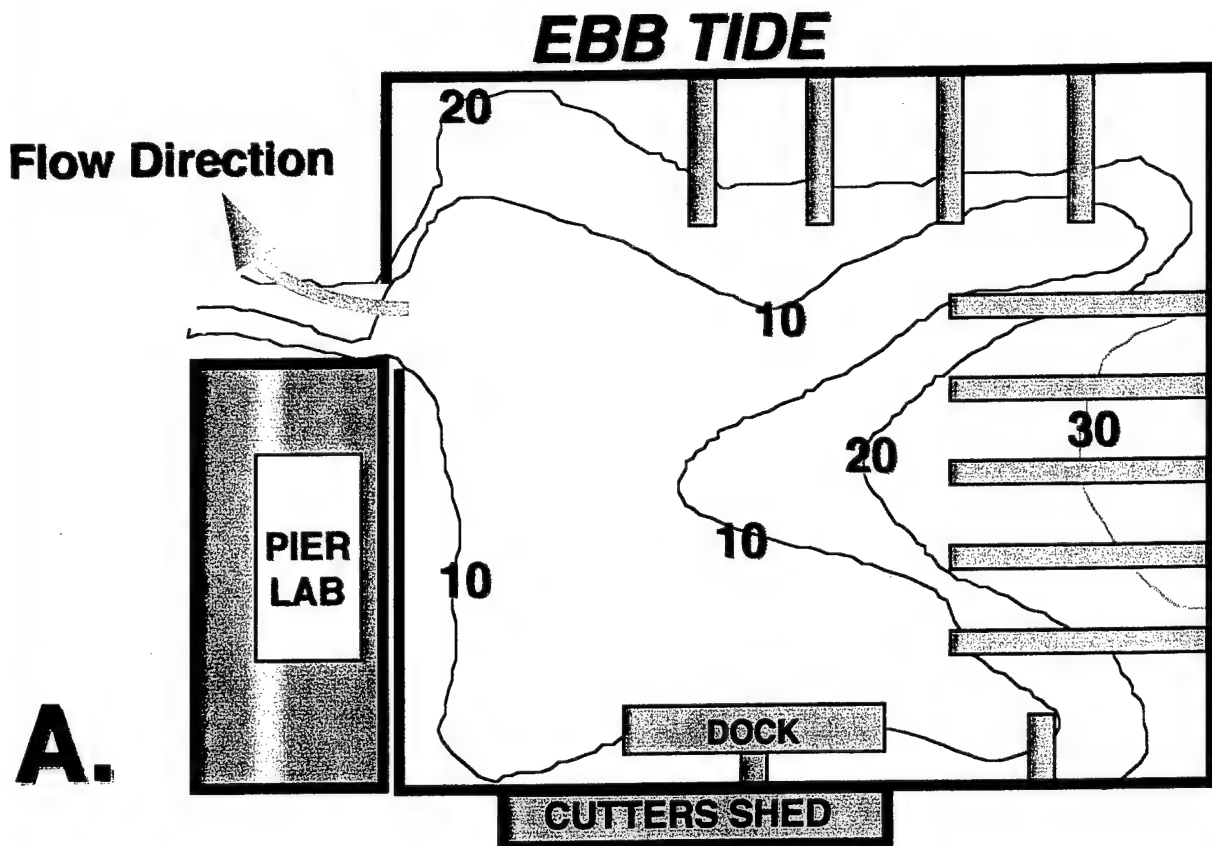


Figure 36.

10
Total Ionic Cu Concentration (ppb)

A.

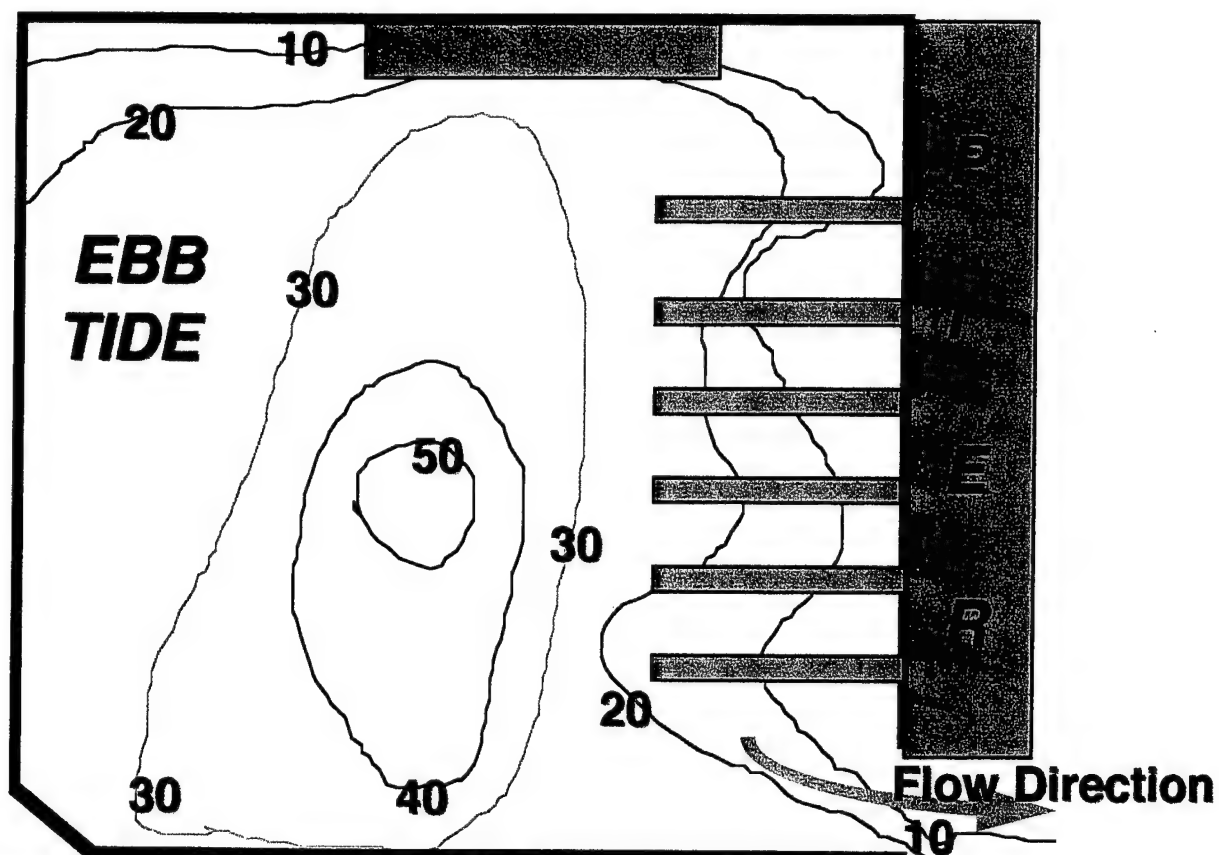
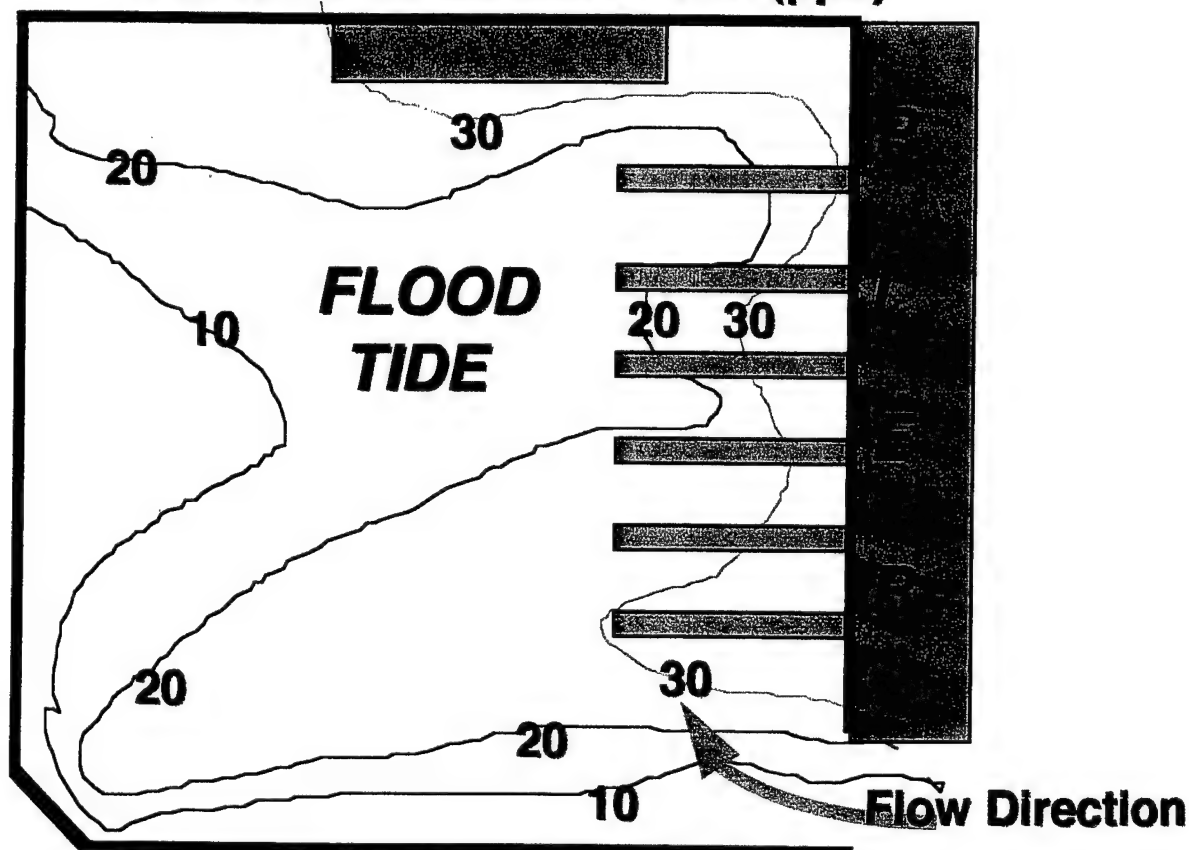


Figure 37.

Total Ionic Cu Concentration (ppb)

B.



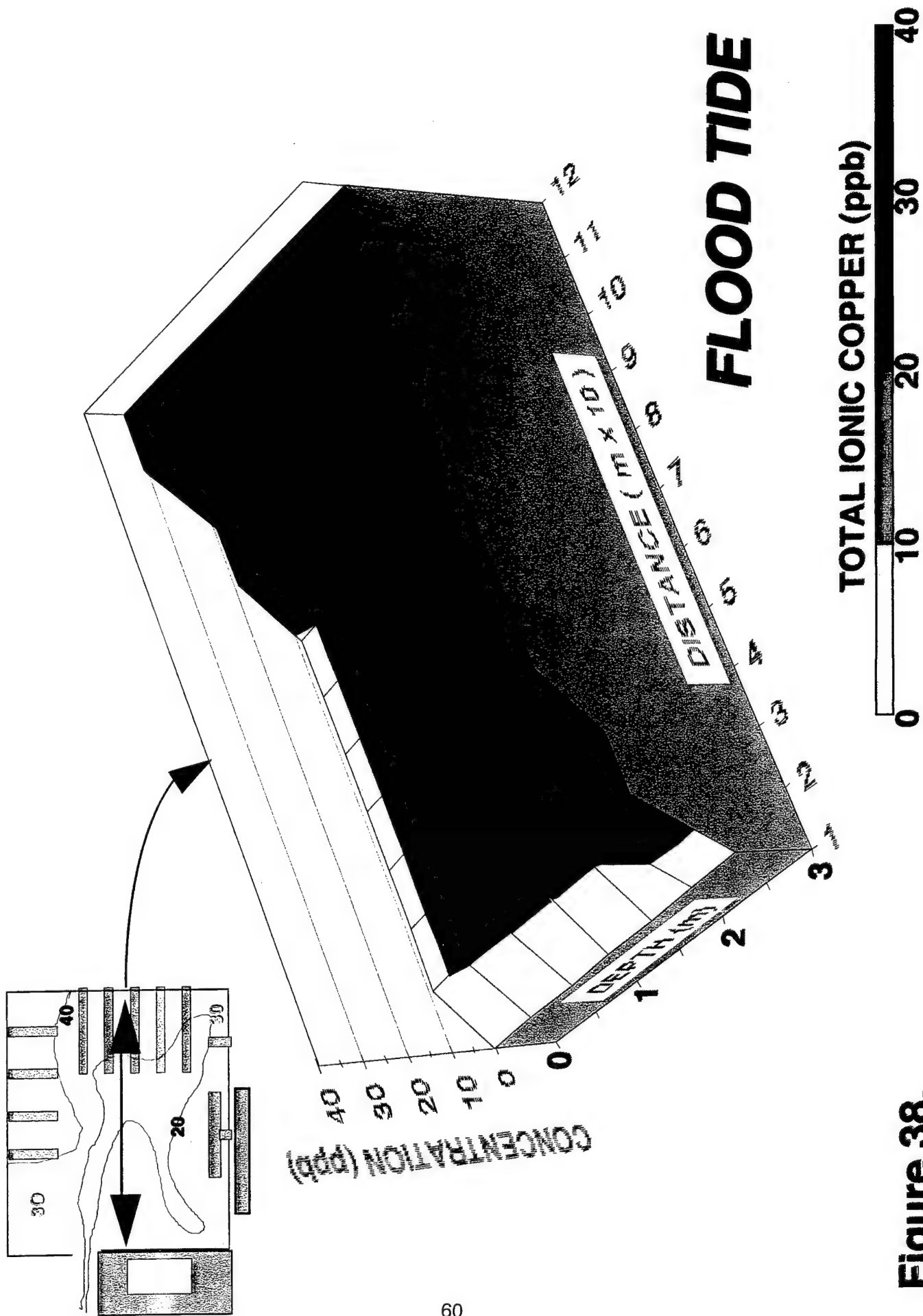


Figure 38.

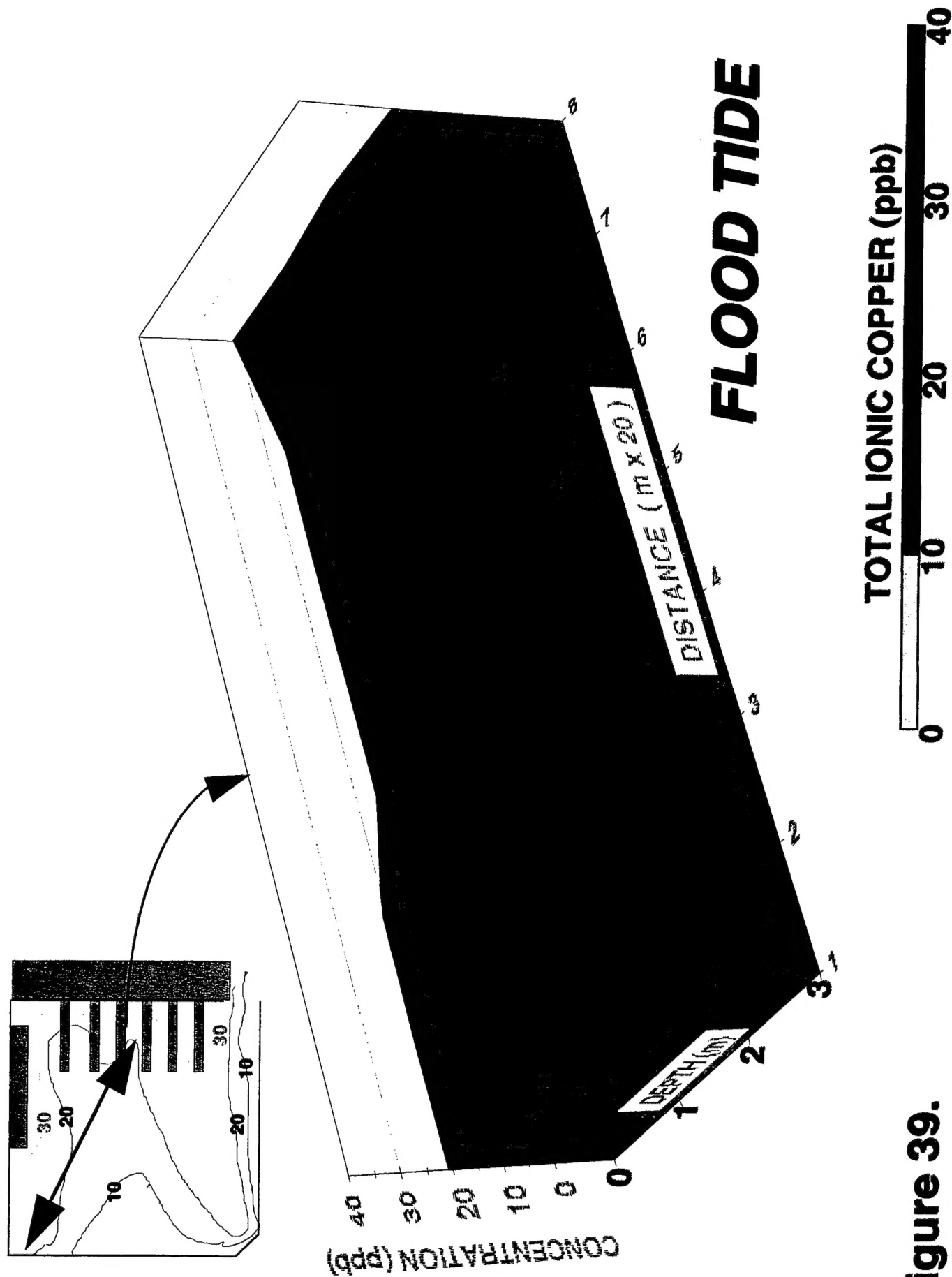
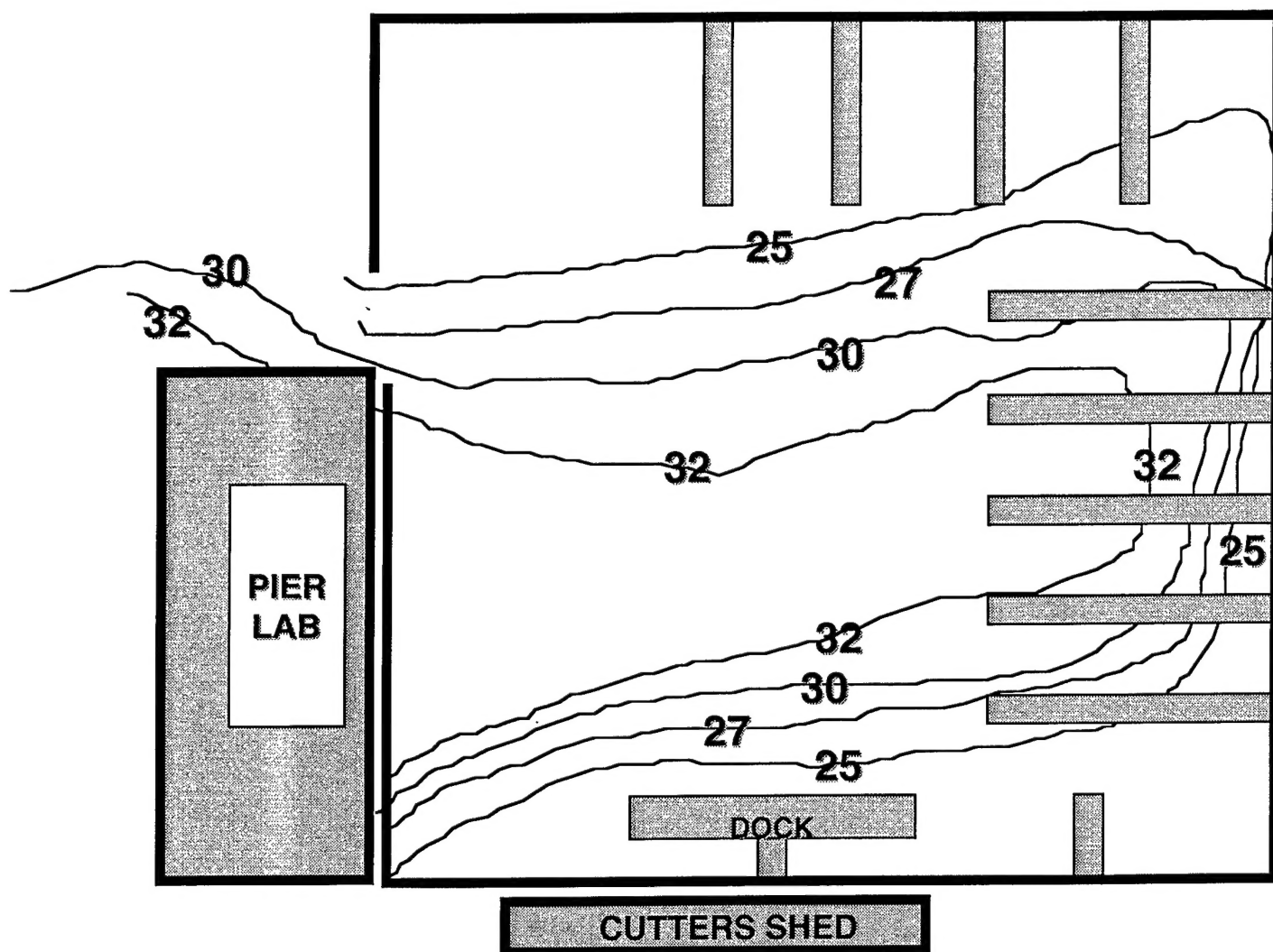
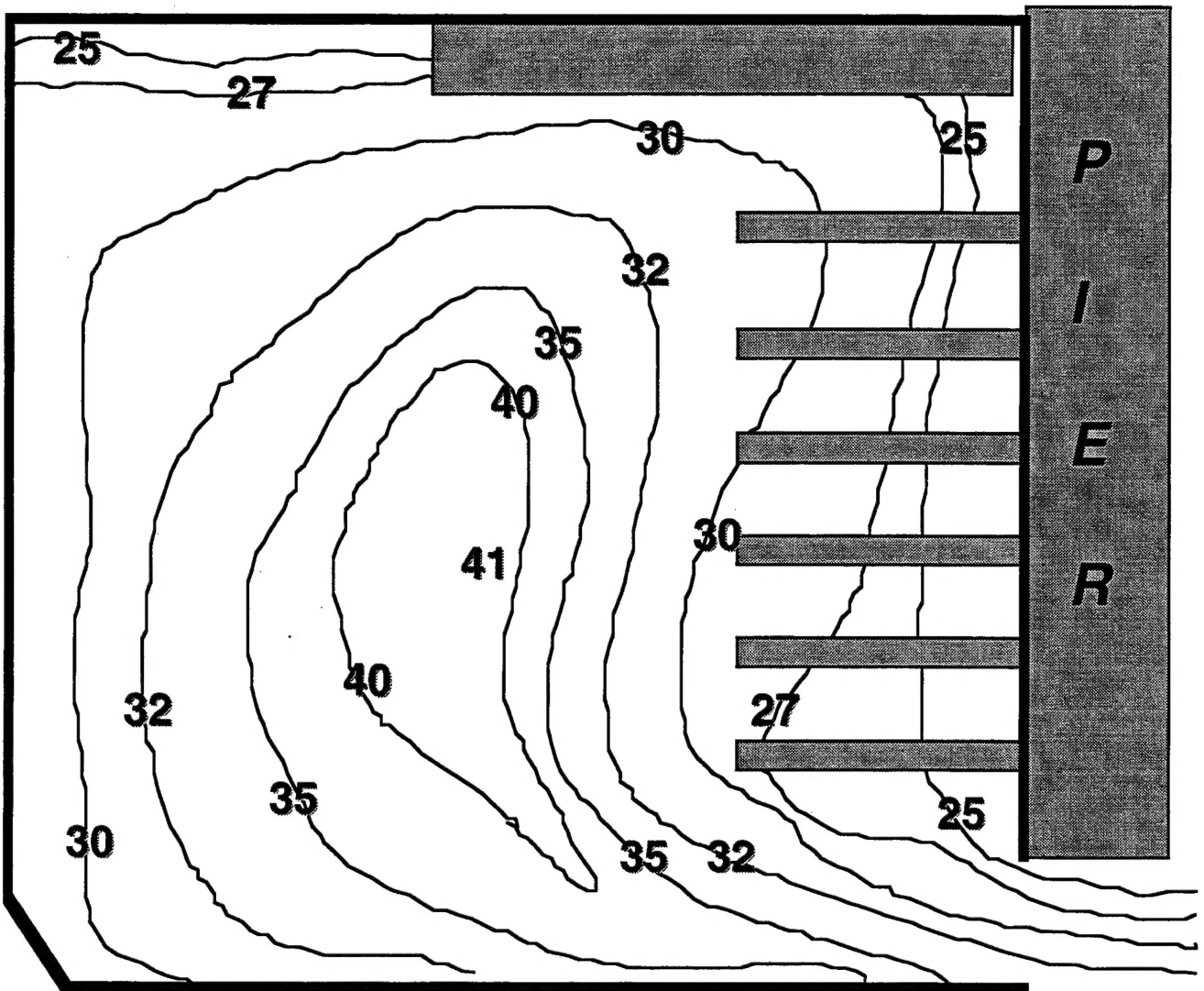


Figure 39.



SANTEE BASIN
PARTICULATE ORGANIC MATER
(mg/L)
FLOOD TIDE

Figure 40.



**NAVY ANNAPOLIS HARBOR
PARTICULATE ORGANIC MATER
(mg/L)
FLOOD TIDE**

Figure 41.

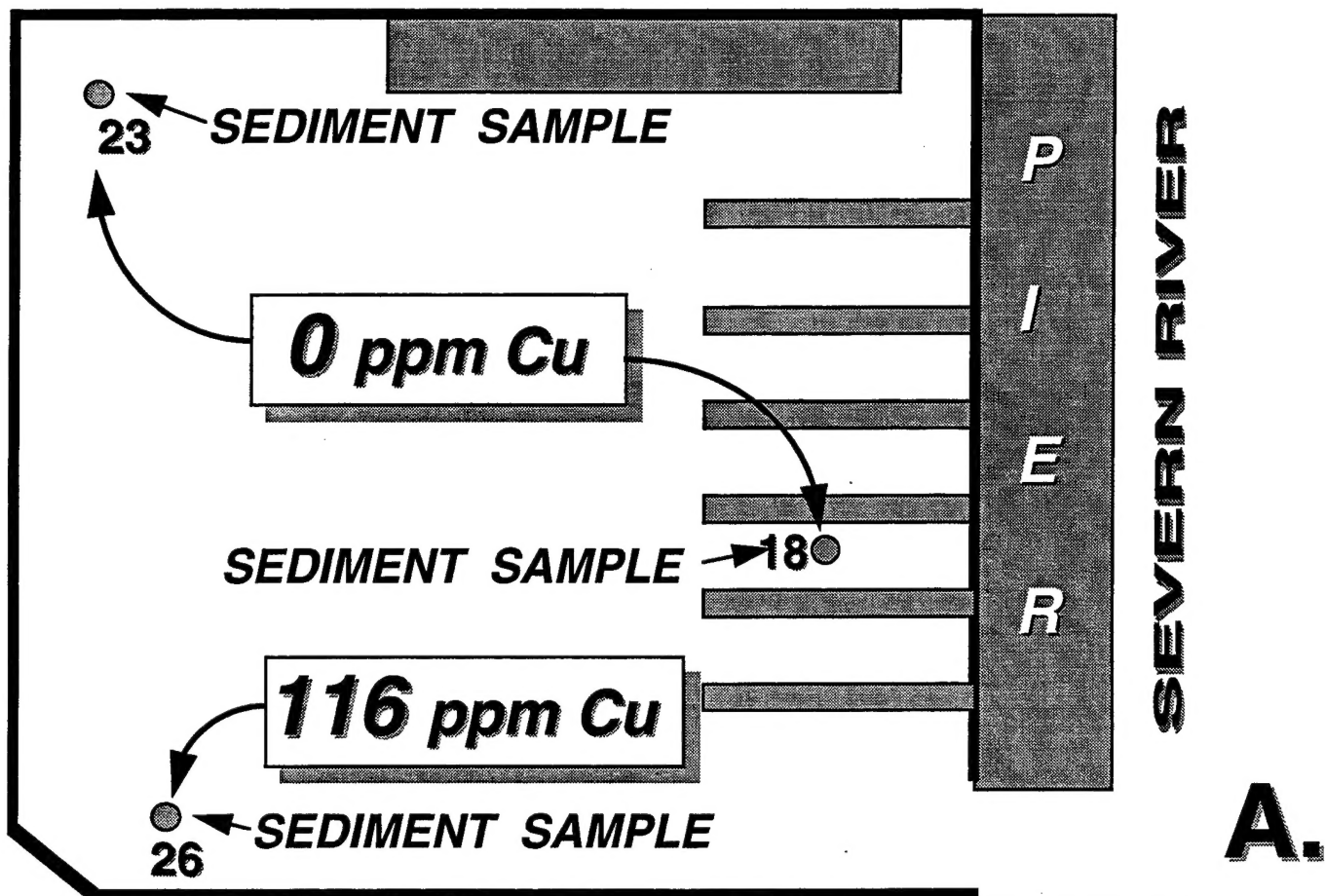


Figure 42.

